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Changes of State

A MATHEMATICAL-PHYSICAL ASSESSMENT

Dedicated

to the memory of

RALPH FOWLER

Changes of State

A Mathematical-Physical Assessment

by

H. N. V. TEMPERLEY, M.A.

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Preface

My interest in phase transitions was originally aroused by the lectures and personal influence of the late Sir Ralph Fowler to whom I owe an immense debt. The main reason for writing this book was the desire to help actual and potential research workers to "find their way around" this fascinating but complicated field. Although some of the topics, such as superconductivity and ferromagnetism, have been thoroughly dealt with in other books and review articles, much of the information on others, such as fusion and evaporation, has to be sought in original papers, scattered in many journals, often under unexpected titles. Perhaps as a result of this, the basic resemblances between apparently unrelated types of transition have only come to light gradually during the course of many years. It seems opportune to call attention to some of these resemblances and, at the same time, to try to pin-point the individual peculiarities of each type of transition.

Another reason for surveying this field is that study of it raises, in an acute form, the question of what constitutes a "physically acceptable theory". In this field, it is not always good enough to find a plausible model that can be made to agree numerically with the observed facts. I make no claim to have formulated valid additional requirements in words; I shall be content if I have succeeded in calling attention to this question and in illustrating it by some examples. A quite different reason for trying to present a connected account of this subject at the present time is that some recent developments have suggested mathematical problems in fields hitherto regarded as quite "pure", such as double limit problems, partition theory and lattice point and random-walk problems. A selection of such problems has been discussed in the hope that this may stimulate the interest of pure mathematicians.

When a good, readable and accessible account of a particular topic exists elsewhere, I have not hesitated to be very brief. I have surveyed some current controversies and, when I have taken sides, have tried hard to be fair to opposing views. The bibliography accompanying each chapter is nothing like complete. What I have aimed at is to give a representative selection of original papers that I should advise anyone to master before he contemplated doing original work on the corresponding type of transition. The selections have been made in the light of over fifteen years' experience in research work and in guiding the work of others, and I have then tried to weave each such set of papers into a connected account of each type of transition. A reasonably complete bibliography of this whole field would not only fill many hundreds of

pages, but would defeat the basic object I had in mind. Any worker requiring a good bibliography on a special topic could compile it from the many survey articles that I have quoted. I hope, therefore, that no one will feel slighted if I seem to have ignored his work, or to have dealt with it in a wrong perspective.

I should like to express my thanks to the many kind friends who have helped me directly or indirectly. Everyone who has discussed these topics with me, or has corresponded with me about them, has had some influence on the book, and a complete list of names would be very long. At the risk of seeming invidious I should like especially to thank Professors J. G. Kirkwood, Lars Onsager and (the late) Fritz London; Professor G. S. Rushbrooke (who read the proofs and made various suggestions) and Dr. D. Shoenberg for help and guidance on innumerable occasions. My thanks go also to my eight research students, Drs. R. B. Dingle, A. R. Fraser, P. J. Price, O. Penrose, C. G. Kuper, D. H. Trevena, D. W. S. Sciama and I. D. Gurney, for keeping me abreast with developments in their fields, and for setting me right on many other points. I cannot refrain from adding a word of encouragement to younger workers everywhere, on whom the future of the subject depends, particularly to those who feel that their efforts meet with ridicule and obstruction from people in key positions. I have had a very full share of such treatment, from a few people who should have known better, but it so happens that the net result of their efforts was to advance, perhaps by years, the actual completion of this manuscript.

I must express gratitude to the following bodies for grants and stipends that made this work possible: King's College, Cambridge (Studentships, Fellowship, Grants from Research Fund); Leverhulme Foundation (Research grant); Royal Society of London (Smithson Fellowship); Cambridge University (Smith's Prize, Lectureship): United States Congress (Smith-Mundt grant for research at Yale); University of Nebraska (Visiting Professorship).

It has been possible to take account of some developments down to 1955. Portions of the actual writing were done at Cambridge and at Yale but the major part at the University of Nebraska. I would like to thank the typists there, particularly Mrs. Lucy Wheeler and her assistants, for their patience with my difficult scripts.

I have assumed that the reader is familiar with elementary quantum mechanics and with the material covered in Rushbrooke's *Statistical Mechanics*. I am solely responsible for any expressions of opinion, and should particularly like to be told of errors, whether of fact or interpretation, or obvious slips and misprints.

Grantchester, Cambridge, January 1956 H. N. V. TEMPERLEY

Principal Symbols

in approximate order of use

C, C_p, C_v, C_H Heat capacities. (Suffix shows variable kept constant.)

E Internal energy

F Helmholtz free energy $(=E-TS)$

S Entropy

Q Quantity of heat

L Latent heat

V Volume

G' "Magnetic Gibbs function" $(=E-TS+PV-HIV)$

G Gibbs function $(=E-TS+PV)$

The above nine symbols when in italic caps. refer to whole assembly; in italic lower-case to an assembly containing one mole or unit mass.

P Pressure

T Absolute temperature

ρ Density

H Magnetic field

I Intensity of magnetisation

B Magnetic induction

μ Magnetic moment per atom; μ_r defined on p. 161, Chap. VI

x_i General symbol for extensive thermodynamic variable

P_i General symbol for intensive (force) thermodynamic variable

E_{ik}, V_{ik}, U_{ik}, D Defined on p. 16, Chap. II

f Partition function

E_r, ϵ_r rth energy level

g_r, $g(r)$ Multiplicity of rth energy level

$g(r)$, g_2, g_3, etc. Distribution functions. Chap. IV, pp. 53-7

h Planck's constant

k Boltzmann's constant

R Gas constant

S Degree of order in alloy

S, $\mathcal{J}$ Spin and total quantum numbers of atom

S Entropy

a, b van der Waals's constants

B, C Second and third virial coefficients. Chap. IV, p. 63

U Activation energy. Chap. III, p. 33

A Quantum mechanical operator corresponding to an observable. Chap. III, p. 38

$A(t)$ Physical quantity corresponding to **A**

$B(\omega)$ Fourier transform of $A(t)$

Π Peltier coefficient; "Two-dimensional pressure". Chap. VI, p. 129

σ Thomson coefficient

σ Surface energy of liquid

Ψ Schrödinger wave function

Ψ Laplace surface-tension function. Chap. IV, p. 67

ϕ_n Time-independent Schrödinger wave function

δ Dirac delta function

Δx Discontinuity in variable x

Δ Surface energy of superconductor. Chap. IX, p. 272

∇ "Nabla" operator

ν Characteristic frequency of an assembly; $\omega = 2\pi\nu$

d Dimension of an assembly

λ Inverse time constant of an assembly. Chap. III, p. 40

λ Degeneracy parameter of assembly in statistical mechanics

λ Magnetostriction coefficient

λ Parameter occurring in London theory. Chap. IX, p. 253

λ-point Characteristic temperature associated with transition in which latent heat is absent

λ-phenomenon Particular kind of transition (defined in Chap. VIII) associated with a λ-point

x, z Defined in Chap. III, p. 47

θ Statistical temperature. Chap. III, p. 43

θ Degree of adsorption. Chap. VI, p. 130

T Kinetic energy

V, w Potential energy

p Momentum

$f(r)$, $\alpha(r)$, $\phi(r)$, ϵ Parameters occurring in Born and Green's theory; defined in Chap. IV, p. 59

$\beta(r)$ Defined in Chap. IV, p. 59

χ, χ_0 "Smoothed potential" of a liquid. Chap. IV, p. 72

χ, χ_s, χ_0 Adsorption energy

χ Magnetic susceptibility

$Q(T)$ Configurational integral. Chap. IV, p. 78

f_{ij} Mayer function. Chap. IV, p. 78

b_l Cluster integral. Chap. IV, p. 79

β_k Irreducible cluster integral. Chap. IV, p. 83

Z Mayer fugacity. Chap. IV, p. 81

I, α_g, β_g, F_g Parameters occurring in Becker-Döring theory referring to drop containing g molecules. Chap. IV, pp. 91–2

Θ Debye temperature of assembly

M, $\overline{M}$ Total magnetic moment of assembly

ν, $\nu_{1,1}$, $\nu_{1,2}$, etc. Energy constants. Chap. VI, p. 125

ϵ Parameter occurring in Bethe's theory. Chap. VI, p. 143

x_1, x_2; y_1, y_2, y_3; $z_1 \ldots z_6$ Parameters occurring in Kikuchi's theory. Chap. VI, p. 154

$p_{h,k,l}$, α_i Parameters occurring in Zernike's theory. Chap. VI, p. 155

H, K, L, M, μ_k, f, g, ϕ, ψ, χ Parameters occurring in theory of Ising model; defined in Chap. VI, pp. 160–2

$\mathbf{I}$, $\mathbf{C}_r$, $\mathbf{S}_r$ Operators defined in Chap. VI, p. 164

$\mathcal{J}$, $\mathcal{J}_{k,l}$ Exchange integrals. Chap. VII, pp. 182, 186

$\mathcal{J}$ Total quantum number of atom

η Exchange energy. Chap. VII, p. 186

k_ν, κ_ν Parameters occurring in Bloch theory. Chap. VII, pp. 186–7

C_1, C_2 Velocities of first and second sound in liquid helium. Chap. X, pp. 164–5

$\mathbf{E}$ Electric field vector $\mathbf{H}$ Magnetic field vector

$\mathbf{J}_s$ Current vector associated with "superconducting" electrons. Chap. IX

$\mathbf{J}_n$ Current vector associated with "normal" electrons. Chap. IX

Γ Rate of conversion of superfluid. Chap. X, p. 290

$S(K)$ Fourier transform of function $g(r)$ defined in Chap. IV, p. 53; first mentioned in Chap. X, p. 314

NOTES ON TERMINOLOGY

Unless another meaning is obvious, the expression "thermodynamic potential" refers collectively to functions such as the Helmholtz or Gibbs free energies.

The words "partition", "partition function" are used in their statistical mechanical and *not* their pure mathematical senses.

The word "state" is *not* used in its quantum-mechanical sense, the expression "energy-level" being used instead. In a statistical mechanical context the word "state" implies the same as what some writers have expressed as "complexion".

A "system" implies an elementary entity (e.g. atom, molecule, photon) that makes up an "assembly". An "ensemble" is a hypothetical collection of identical assemblies.

CHAPTER I

Historical Introduction

1.1. Early Theories

It seems to have long been recognised that pure substances melt and boil at sharply defined and reproducible temperatures; the routine use by chemists of a melting-point determination, as a means of identifying a substance and checking its purity, is probably of great antiquity. The first step towards an understanding of the underlying mechanism of a change of state was taken by Joseph Black in the eighteenth century, for he seems to have been the first person to state clearly that heat is used up when ice melts. With the improvement in calorimetric methods it gradually came to be realised that such transitions as, for example, those of rhombic to monoclinic sulphur, of mercuric iodide from the red to the yellow form, of quartz from the α to the β variety could be associated with definite transition temperatures, and might involve the absorption of latent heat or be accompanied by anomalies in other quantities such as the specific heat and coefficient of expansion.

One may group together all observable physical changes in the structure of matter that are associated with a definite transition temperature as "changes of state". As usual, it is difficult to frame a precise definition, as we want to exclude chemical changes and processes not associated with any definite temperature, such as thermal expansion, and yet to include processes such as the melting of glasses, which are spread over a small range of temperature however pure and homogeneous the sample. Until comparatively recent times the underlying similarities of all changes of state have not been realised, and theoretical developments consisted of attempts to understand individual cases. The first definite theory of a change of state was due to van der Waals, who showed that a crude attempt to take account of the interactions between molecules and their finite sizes led logically to the prediction of the liquefaction and critical phenomena that occur in actual gases. It is not usually possible to choose the van der Waals constants a and b so as to give anything better than "order of magnitude" agreement with experiment, but, as we shall see below, this is all that can be expected. Among other early theories of a change of state may be mentioned the Weiss theory of ferromagnetism (1907). Here again, the interaction between atomic magnets is allowed for only very crudely, but the theory can nevertheless be relied on quantitatively in many respects. A little later,

Lindemann (1910) developed a crude theory of fusion, the basic idea behind which has been extended and refined by various later workers, notably Lennard-Jones and Devonshire (1939). The next great advance was due to Heisenberg (1928), who showed that the large interaction between atomic magnets that was needed by Weiss's theory of ferromagnetism received a natural explanation on the basis of wave-mechanics.

1.2. Later Developments

In 1934 Bragg and Williams showed that the appearance of an ordered structure in an alloy such as β brass could be explained on lines broadly similar to those of Weiss's theory of ferromagnetism, by postulating slightly different interactions between like and unlike atoms, and similar ideas have since been applied to quite a number of other phenomena, such as adsorption phenomena and the penetration of gases into metals, see Fowler and Guggenheim (1939), the so-called λ-anomaly in solids, Fowler (1935), the theory of solutions and critical mixing of liquids, see, for example, Fowler (1936), the appearance of spontaneous electric polarisation in bodies such as Rochelle salt, Fowler (1935). As was only to be expected, some of the theories that emerged during this very fruitful period have since been challenged and, while it has not yet been shown that any of them are wrong in principle, it has become clear that some of them are too crude to give more than a description of the facts in broad outline, of which some are not even reproduced qualitatively.

The difficulty about assessing such theories is that one can either attempt, as in the Weiss theory of ferromagnetism, to represent the effect of intermolecular interactions by a single parameter; or one can attempt a more detailed theory. In the latter case, however, one faces the familiar difficulty that the theoretical formulae to be compared with experiment contain a number of parameters that cannot be calculated—so-called "adjustable constants"—and it is difficult to decide at what stage a theory containing two such constants is "better" than one containing only one. It is perhaps significant that a somewhat different theoretical trend became apparent in 1938.

1.3. Attempts at Rigorous Theories, using Simplified Models

The attempt was made to proceed from an assumed form of intermolecular interaction to predictions of the thermodynamic properties of an assembly by a mathematically rigorous argument. The results have been encouraging enough to stimulate further progress, although, so far we possess only five theories of this new type:

(a) In 1938 Mayer showed that the assumption that the molecular interaction function included an attractive and a repulsive term had, as a

rigorous consequence, the appearance of a singularity in the free energy at and below a certain temperature (provisionally identified with the critical temperature of the gas). There seems to be no doubt that this conclusion is correct, but the mathematical nature of the singularity is still not known for certain, in spite of much further work.

(b) In 1938 F. London showed that the requirements of wave-mechanics implied the existence of a transition temperature in an assembly of molecules described by symmetrical wave functions even if the intermolecular interactions were vanishingly small, and he suggested that this result might be connected with the properties of liquid helium.

(c) In 1941 Landau showed that an assembly in which the effects of intermolecular interaction were satisfactorily represented by Debye waves would have strange properties at sufficiently low temperatures, which he also suggested might be connected with those of liquid helium.

(d) In 1944 Onsager deduced that a plane square lattice of atomic magnets each capable of only two orientations, in which interactions were supposed to occur only between nearest neighbours, would have a transition temperature. Later work shows that such a model also shows spontaneous magnetisation, and that similar results almost certainly hold in three dimensions. See p. 160.

(e) The Weiss (1907) and Bragg-Williams (1934) theories follow as a rigorous consequence of the assumption that the molecular interactions are *independent of distance* (extreme long-range interactions). See p. 122, also Temperley (1954) on the limiting process needed.

It is certainly true that no assembly conforming to types (b), (c), (d), or (e) actually exists, nevertheless a comparison of the thermodynamic consequences of such extreme assumptions gives one a clearer idea of what are likely to be the consequences of any *actual* interaction. For example, in a ferromagnetic we are now in a position to compare the consequences of assuming that the interaction is of *very long* range with those of assuming that it is of *very short* range. The consequences of these two extreme assumptions are sufficiently alike to enable tentative conclusions to be drawn about the relationship between the thermodynamic properties of an assembly and the form of the interaction function.

1.4. Thermodynamic Approach

As an alternative to attempting a detailed theory of a change of state, which, owing to mathematical difficulties, is at present possible only in rough outline, or at the expense of extreme idealisation of the model, one may introduce a purely thermodynamic classification of changes of state. In other words, we do not tackle the difficult question of precisely

what feature of the intermolecular interaction is responsible for, e.g. the form of the specific heat anomaly associated with a given change of state, but instead we attempt to deduce as much as we can about a change of state without assuming anything at all about the *mechanism* responsible for it. The first step towards such a classification was the Clausius-Clapeyron equation, which established a relation between the latent heat and change of density occurring as a result of, for example, fusion or evaporation—in fact an analogous treatment applies to any change of state in which a latent heat is involved. Gradually it was realised that certain changes of state take place without any latent heat, in which case the Clausius-Clapeyron equation becomes worthless, but no further advance was made in the general theory until 1933, when Ehrenfest introduced the idea of "phase-changes of the second order"—that is, transitions that involve a discontinuity in the specific heat but no latent heat. It was for some time thought that a complete classification of change of state, of various degrees of "abruptness", could be based on this idea of the "order" of a transition, but Tisza (1949, 1951) has shown that such a classification is incomplete, and that certain types of transition exist that are not covered by Ehrenfest's scheme. Further, Tisza's work has directed attention to an important possibility, the occurrence of a change of state without the traditional accompaniment of a specific heat anomaly, though no definite instance of this is yet known for certain.

1.5. Irreversible Effects accompanying Changes of State

Every change of state involves a finite change in some of the thermodynamic properties, and this both occupies time and is necessarily accompanied in practice by thermodynamically irreversible effects. These are of great, almost bewildering, variety, and each change of state possesses its own set of accompanying irreversible effects and other secondary phenomena. Our state of knowledge of these varies widely, ranging from ferromagnetism, where very complete theoretical and experimental investigations have been made, to the apparently quite different case of ferroelectricity, where the approach is at present purely empirical. Many attempts have been made to set up thermodynamical treatments of irreversible processes, but apart from the pioneer work of Onsager (1931) development has been very slow until quite recent times, when the question has been taken up by quite a number of workers.

In the ensuing chapters, we shall deal first with the thermodynamic classification of changes of state, secondly with a general theoretical discussion, and lastly with a more detailed consideration of some of the phenomena about which most is known.

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CHAPTER II

Classification of Changes of State

2.1. The Condition of Equilibrium between two Phases

We now investigate the conditions of equilibrium between two chemically identical but physically distinguishable phases, e.g. liquid and vapour, two types of crystal structure, the ordered and disordered forms of an alloy, or the two forms of liquid helium. For the purposes of this chapter we imagine that the changes envisaged are carried out so slowly that they may be treated as thermodynamically reversible. It is not always sufficiently emphasised that these two concepts of *dynamic equilibrium* and *thermodynamic reversibility* are closely connected. Suppose, for example, that we take an assembly consisting of a vessel containing liquid and vapour. If the pressure and temperature lie on the vapour-pressure curve, so that equilibrium between the two phases is possible, it is then, and only then, permissible to think of such a process as changing a very small quantity of liquid into vapour at constant pressure and temperature as being, at least in principle, possible to perform in a reversible manner. Clearly, if the two phases are *not* in equilibrium, the envisaged process either cannot be performed at all, or else will involve a finite quantity of material and will proceed in an essentially irreversible fashion, like the "bumping" of a liquid when it is heated in a very smooth flask. One can never actually *perform* a truly reversible process even if two phases are in equilibrium, but it is a reasonable deduction from experimental facts that we reach correct conclusions by postulating the "possibility in principle" of such processes. The reader is referred to textbooks of thermodynamics for further discussion of this point.

Let us now suppose that we have determined a point (P_0, T_0) on the pressure temperature diagram at which the two phases are in equilibrium, and we wish to determine the form of the equilibrium curve in the neighbourhood. We examine the effect of a mass dm of substance changing reversibly from one phase to the other. For any infinitesimal change we have, by the two laws of thermodynamics,

$$dE = T dS - P dV \qquad (1)$$

If matters are arranged so that the pressure and temperature are kept constant, the corresponding result is

$$dG = d(E - TS + PV) = dE - T dS - S dT + V dP + P dV = 0 \qquad (2)$$

that is, the Gibbs free energy for the whole assembly is constant for such a change. The result of such a change is that the mass of one phase increases by dm, while that of the other phase decreases by the same amount. Now, since P and T are supposed to be constant, and internal energy, volume and entropy are then additive quantities, the Gibbs free energy of the whole assembly is the sum of the Gibbs free energies of the two phases. (Internal energy and volume can always be added together, while no change in total entropy occurs if two phases *in equilibrium* are brought together.) Thus, our condition for equilibrium becomes

$$0=\mathrm{d}m\left(\frac{\partial G}{\partial m_1}\right)_{P,\,T}-\mathrm{d}m\left(\frac{\partial G}{\partial m_2}\right)_{P,\,T} \quad \text{or} \quad g_1=g_2 \tag{3}$$

where g_1 and g_2 are the Gibbs functions per unit mass for the phases 1 and 2—the so-called partial or chemical potentials.

2.2. Applications of Equation (3)

Equation (3) is the fundamental condition of equilibrium between two phases, and, if we possessed explicit expressions for the variations of g_1 and g_2 with pressure and temperature, we could use them to draw the equilibrium curve. In practice we often do not have this information and must proceed indirectly. Equation (3) must be satisfied at the point ($P=P_0$, $T=T_0$) which we have supposed to be part of the equilibrium curve. We now attempt to determine a point ($P_0+\mathrm{d}P$, $T_0+\mathrm{d}T$) in the neighbourhood of this known one. Expanding by Taylor's theorem—the legitimacy of which process we shall discuss below, we get

$$g_1(P,T)=g_1(P_0,T_0)+\mathrm{d}P\left(\frac{\partial g_1}{\partial P}\right)_T+\mathrm{d}T\left(\frac{\partial g_1}{\partial T}\right)_P+ \frac{(\mathrm{d}P)^2}{2}\left(\frac{\partial^2 g_1}{\partial P^2}\right)_T+\frac{(\mathrm{d}T)^2}{2}\left(\frac{\partial^2 g_1}{\partial T^2}\right)_P+\mathrm{d}P\mathrm{d}T\left(\frac{\partial^2 g_1}{\partial P\partial T}\right)+\ldots \tag{4}$$

with a precisely similar equation for g_2. We know that $g_1(P_0\,T_0)=g_2(P_0,T_0)$, since the two phases are in equilibrium at this point, and we have to determine the ratio of dP and dT in such a way that $g_1(P_0+\mathrm{d}P,T_0+\mathrm{d}T)=g_2(P_0+\mathrm{d}P,T_0+\mathrm{d}T)$. A number of different possibilities are now open.

A. There is a finite change in one or both of the differential coefficients $(\partial g/\partial P_T)$, $(\partial g/\partial T)_P$ when the transition occurs.

B. Both of these first-order differential coefficients are continuous and have the same value for both phases.

C. The Taylor expansion (4) becomes illegitimate for one or both phases.

Actual examples of all three of these possibilities are known, and a

sub-classification of possibilities B and C is necessary. We consider the various possibilities in turn:

2.3. Classification of Transitions into Thermodynamic Types

A. We recall that $(\partial g/\partial P)_T=v$, the volume of unit mass, and a discontinuity in this quantity implies that the transition is accompanied by a finite change of density. Also, $-(\partial g/\partial T)_P=s$, where s is the entropy per unit mass, and a discontinuity in this quantity at the transition implies a finite *latent heat*, for if a latent heat l per unit mass is taken in reversibly during the transition, the corresponding entropy change is l/T. Thus, in order that $g_1=g_2$, at the point $(P_0+\mathrm{d}P,\ T_0+\mathrm{d}T)$ equation (4) shows us that we must have

$$\frac{\mathrm{d}P}{\mathrm{d}T}=-\left[\frac{\partial g_1}{\partial T}-\frac{\partial g_2}{\partial T}\right]\Big/\left[\frac{\partial g_1}{\partial P}-\frac{\partial g_2}{\partial P}\right]=\frac{(s_1-s_2)}{(v_1-v_2)}$$

the terms of higher order in $\mathrm{d}P$ and $\mathrm{d}T$ being negligible as long as at least one of the expressions in square brackets is finite. This gives us:

$$\frac{\mathrm{d}P}{\mathrm{d}T}=\frac{l}{T(v_1-v_2)}=\frac{s_1-s_2}{v_1-v_2} \tag{5}$$

This is just the Clausius-Clapeyron equation, in which the slope of the transition curve is related to the latent heat of the transition and to the change of density. It has been carefully checked experimentally, and is, as far as we know, always accurate. Only two cases seem to be known for which $\mathrm{d}P/\mathrm{d}T$ vanishes at a finite temperature. These are for the transitions ice I to ice III and benzene I to benzene II. Tammann and Mehl (1925) *States of Aggregation*, pp. 164, 190. A third suspected case is the solidification of He_3, Weinstock, Abraham and Osborne (1952), Temperley (1954 b). Some pairs of partially miscible liquids, e.g. nicotine and water, have mixing curves that behave in the same way.

B. If there is no latent heat of transition, and no change of density, equation (5) becomes indeterminate. We must return to equation (4), which shows us that we can get an equation for the ratio $\mathrm{d}P/\mathrm{d}T$, giving us the slope of the transition curve passing through the point $(P_0,\ T_0)$, if at least one of the *second* differential coefficients of g with respect to the variables P and T takes different values for the two phases. We may write:

$$0=g_1-g_2=\frac{(\mathrm{d}P)^2}{2}\left\{\left(\frac{\partial^2 g_1}{\partial P^2}\right)_T-\left(\frac{\partial^2 g_2}{\partial P^2}\right)_T\right\}+\frac{(\mathrm{d}T)^2}{2}\left\{\left(\frac{\partial^2 g_1}{\partial T^2}\right)_P-\left(\frac{\partial^2 g_2}{\partial T^2}\right)_P\right\}+$$
$$\mathrm{d}P\mathrm{d}T\left\{\left(\frac{\partial^2 g_1}{\partial P\partial T}\right)-\left(\frac{\partial^2 g_2}{\partial P\partial T}\right)\right\}\ldots \tag{6}$$

Now $(\partial^2 g/\partial P^2)_T=(\partial v/\partial P)_T$ and a discontinuity in this quantity

implies a discontinuity in the isothermal compressibility. $(\partial^2 g/\partial T^2)_P = -(\partial s/\partial T)_P = -c_p/T$ and a discontinuity in this quantity implies a discontinuity in the specific heat at constant pressure, while the mixed derivative $\partial^2 g/\partial P \partial T$ is equal to $(\partial v/\partial T)_P$ and a discontinuity in this implies a discontinuity in the coefficient of expansion. It would be *possible* to have a transition in which all three of these second differential coefficients were continuous, the first discontinuity occurring in some still higher derivative. Such a situation would be extremely difficult to detect experimentally, because what are, in fact, usually observed experimentally are variations of *volume* and *heat content* with temperature and pressure, so that the plotting of such a curve as that of *compressibility*, *specific heat* or *coefficient of expansion* already involves one *numerical differentiation* of the experimental results. It is well known that experimental errors are accentuated by this process, and it would, in practice, be extremely difficult to decide whether, for example, the temperature coefficient of the compressibility or of the specific heat was continuous or discontinuous at the transition temperature if the compressibility or specific heat itself were continuous. The scatter of experimental points always seems, quite understandably as we shall see below (p. 41), to be greatest near the transition temperature—just where the greatest accuracy is required. There is often uncertainty about the exact position of the transition temperature itself, which adds to the difficulty of analysing the experimental data numerically.

We shall therefore consider only the case where one or more of the second derivatives of g is supposed to be discontinuous. A transition of this kind was named by Ehrenfest (1933) *a transition of the second order*, one involving latent heat for which equation (5) holds being called a transition of the first order, while the hypothetical transitions for which both first derivatives and all three second derivatives of g are continuous through the transition, may be called transitions of the third (or higher) orders. Ehrenfest overlooked that his "transitions of the second order" might be of two distinct types, and we shall give an improved version of his treatment below.

Type 1. $(\partial g/\partial P)_T$ and $(\partial g/\partial T)_P$ are continuous not only at the point (P_0, T_0) but also *along a finite length of the equilibrium curve*. The condition that $(\partial/\partial P)(g_1-g_2)=0$ at the point $(P_0+\mathrm{d}P, T_0+\mathrm{d}T)$ as well as at (P_0, T_0) is that

$$\mathrm{d}P\frac{\partial^2}{\partial P^2}(g_1-g_2)+\mathrm{d}T\frac{\partial^2}{\partial P\partial T}(g_1-g_2)=0 \qquad (7)$$

Similarly, the condition that $(\partial/\partial T)(g_1-g_2)=0$ at the point $(P_0+\mathrm{d}P, T_0+\mathrm{d}T)$ as well as at (P_0, T_0) is

$$\mathrm{d}P\frac{\partial^2}{\partial P\partial T}(g_1-g_2)+\mathrm{d}T\frac{\partial^2}{\partial T^2}(g_1-g_2)=0 \qquad (8)$$

As we have just pointed out $(\partial^2 g/\partial P^2)_T$ is connected with the compressibility, $(\partial^2 g/\partial T^2)_P$ with the specific heat, and $\partial^2 g/\partial P \partial T$ with the coefficient of expansion, so that if we eliminate the ratio $\mathrm{d}P/\mathrm{d}T$ between equations (7) and (8) we get Ehrenfest's relation between the discontinuities in these three quantities at the transition

$$-\left\{\left(\frac{\partial v_1}{\partial P}\right)_T-\left(\frac{\partial v_2}{\partial P}\right)_T\right\}\left\{\frac{c_{p(1)}-c_{p(2)}}{T}\right\}=\left\{\left(\frac{\partial v_1}{\partial T}\right)_P-\left(\frac{\partial v_2}{\partial T}\right)_P\right\}^2 \qquad (9)$$

Various attempts were made to check this relation, for example against the data for the transition of liquid helium, see Keesom, *Helium*, Chap. 5, and against data on the λ point anomaly in solids, see Ruhemann, *Low Temperature Physics*, Part II, but it is a matter of considerable difficulty to decide whether an actual discontinuity in a specific-heat curve really exists, and, even if one has convinced oneself that it does, to assign a numerical magnitude to it. This difficulty is particularly serious for "high" and "thin" specific heat anomalies which occur, for example, in ammonium salts. As we shall see below, there is an alternative classification for anomalies of this type. (See Class C below.)

Type 2. $(\partial g/\partial P)_T$ and $(\partial g/\partial T)_P$ are only continuous for a transition at the one point (P_0, T_0), the remainder of the equilibrium curve corresponding to first-order transitions at which these coefficients are discontinuous. In this case, equations (7) and (8) are incorrect, but the weaker statement (6) is still true. It implies a quadratic equation for the ratio $\mathrm{d}P/\mathrm{d}T$ which would correspond to two equilibrium curves, each associated with a first-order transition, crossing at the point (P_0, T_0) at which point alone there would be no latent heat. No such transition is known involving the variables P and T, but a quite analogous situation does occur for the transition of a superconductor to the normal state (Shoenberg, *Superconductivity*, Chap. 3). Here, the relevant pair of variables is H and T, where H is the applied magnetic field, and, instead of the Gibbs free energy, we must work with a so-called "magnetic Gibbs function", which is defined as $g_m=g-HB/4\pi\rho$ where B is the magnetic induction and ρ the density. It is also possible to work with the closely related function $g'=g-MH$ (where M is the magnetic moment per unit mass). Since the work done in magnetising unit mass is $H\mathrm{d}B/4\pi\rho$ we have, by the usual thermodynamic arguments, $(\partial g_m/\partial T)_H=-s$ while $(\partial g_m/\partial H)_T=-B/4\pi\rho$. (Here we are neglecting the effect of the very small volume changes due to magnetostriction.) Now, for a large superconductor, it is an observed fact that B is always zero as long as the metal is superconducting, while, for the normal metal, B is practically equal to H, the permeability being very nearly unity at all temperatures. Differentiating the relation $(\partial g_m/\partial H)_T=-B/4\pi\rho$ with respect to T, we conclude that the mixed second derivative $\partial^2 g_m/\partial H \partial T$ is zero for *both* phases. (B depends on H for the normal metal, but is

still, to a high approximation, independent of T.) Also $(\partial^2 g_m/\partial H^2)_T = -1/4\pi\rho$ for the normal metal, but is zero for the superconductor because $B=0$. Further, it is an observed fact that the transition occurs without latent heat only for $H=0$. We may then substitute the values for the second differential coefficients into the analogue of equation (6) which then gives us

$$0=(\mathrm{d}H)^2\left(-\frac{1}{4\pi\rho}\right)+(\mathrm{d}T)^2\left\{-\left(\frac{\partial s_n}{\partial T}\right)_H+\left(\frac{\partial s_s}{\partial T}\right)_H\right\}$$

or

$$\frac{\mathrm{d}H}{\mathrm{d}T}=\pm(4\pi\rho T\Delta c_H)^{1/2} \tag{10}$$

This equation, connecting the height of the specific heat discontinuity Δc_H with the slope of the transition curve at $H=0$, has usually been derived by taking the analogue of equation (5), which applies when H is finite and the change is of the first order,

$$\frac{\mathrm{d}H}{\mathrm{d}T}=\frac{l(4\pi\rho)}{T(B_n-B_s)}=\frac{4\pi\rho l}{HT} \tag{11}$$

(ρl=latent heat per unit volume) and determining the limiting form of this, when H vanishes, by multiplying both sides of (11) by H, differentiating with respect to T, and then putting $H=0$. The appearance of the ambiguity of sign in equation (10) is connected with the fact that H may be of either sign—thus indeed two transition curves, corresponding to positive and negative H, do cut at a finite angle at the one point $(0, T_0)$ at which the transition is of second order. The size of Δc_H is easier to decide than in other cases, first because there is no noticeable "tail" to the specific heat curve (fig. 1), also because the specific-heat curve for the normal metal can be "extrapolated" below the transition point by applying (before the specific heat determination) a sufficiently large magnetic field to keep the metal normal (dotted curve in fig. 1). The "extrapolated" specific heat curve seems to join smoothly on to the "normal" curve without a field, which gives confidence in the reality of a jump in c_H at the transition. Thus, it seems fairly clearly established that a transition that is of the second order, in the sense of showing a specific heat discontinuity without latent heat, really exists. It is less certain whether or not a transition of Type 1 (that actually envisaged by Ehrenfest) actually exists. Very recent work on liquid helium, Atkins and Chase (1951), Atkins (1953), has thrown doubt on the originally accepted conclusion that its transition was in this category, although it

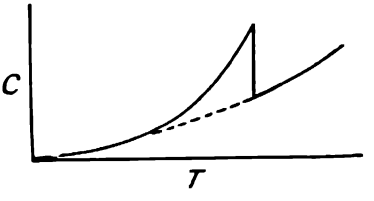

Fig. 1. Specific heat of superconductor.

was for some time thought to be. (See Keesom, *Helium*, Chap. 5, for a discussion of the earlier evidence. See also Kuper (1955).)

C. A third possibility is that a Taylor expansion such as (4) becomes illegitimate as the transition point is approached. This might occur for various reasons—for example:

1. The transition curve might consist simply of the isolated point (P_0, T_0) and no others in the neighbourhood. As far as is known, this situation never occurs, transition curves always being continuous.

2. The transition curve ends at a "stop-point", e.g. the curve $y=e^{-1/x}$ ends abruptly at the origin and *all* the derivatives of y tend to zero there. Very recently Zimm (1951) has suggested that the critical point in a gas may be of this type.

3. Some of the derivatives of g for one or both phases become "infinite" so that the Taylor expansion (4) is no longer valid. This possibility seems to have been first clearly pointed out by Tisza (1949). On physical grounds we can at once rule out the possibility of $(\partial g/\partial P)_T$ or $(\partial g/\partial T)_P$ becoming "infinite" anywhere, as this would imply infinite volume or entropy. There is, however, no reason why one or more of the *second* derivatives of g should not become "infinite", provided that certain obvious physical conditions are satisfied. For example, there is no objection, in principle, to an "infinity" in a specific heat curve, provided that the total heat absorbed during the transition, measured by the "area under the curve", is finite. Equally, it is possible for a coefficient such as $(\partial V/\partial T)_P$ to become "infinite" at one particular pressure and temperature, there being no physical reason why a coefficient of expansion should not become very large at one particular temperature provided that the associated change of volume occurring when we go through this temperature is finite. Thus there is, in principle, no reason why a specific heat or coefficient of expansion should not behave like $|T_0-T|^{-1/2}$ or $\log|T_0-T|$ in the neighbourhood of a transition temperature T_0, because the "area under" such a curve remains finite even if we include T_0 in the range of integration, though this would not be true if the variation were more violent, e.g. like $|T_0-T|^{-1}$. Such anomalies are superposed on the ordinary variation of the quantity with T.

Thus, there is no reason, in principle, why some of the second or higher order differential coefficients of g should not become "infinite" (in the usual statistical sense of increasing without limit as the size of the assembly increases). The existence of such an "infinity" would invalidate Taylor expansions such as (4), and this fact alone is enough to show that Ehrenfest's proposed classification is incomplete. The question now arises whether quantitative relations like (5) or (9) can be deduced for this third type of transition. P. J. Price (1951) has shown that it is possible to draw conclusions about the relative *rates* at which

quantities such as specific heat and compressibility approach their "infinite" values when we approach, for example, the critical point of a liquid. Kuper (1955) has pointed out that equations, formally the same as (7) to (9) above but with a slightly changed physical interpretation, should be applicable to *any* transition without latent heat, even though it is not strictly of Ehrenfest's type. Tisza (1949; 1951) has shown that it is often possible to draw physical conclusions about the mechanism of the transition, beginning from observed facts and these purely thermodynamic considerations.

To fix our ideas, let us consider a liquid near its critical point. It is known experimentally that such an assembly is stable and reproducible, but the stability is, as Tisza puts it, of a "lower order" than in an ordinary assembly. The familiar phenomenon of opalescence at the critical point is an indication that the density may depart appreciably from its mean value over a region comparable in linear dimensions with the wavelength of light, i.e. of the order of 10^{-5} cm, whereas, in an ordinary liquid, the density is effectively uniform for all regions of dimensions greater than 10^{-7} cm. The theory of fluctuations shows that, in an ordinary assembly, the fluctuations of the various thermodynamic variables about their statistical mean values become relatively less and less important as the assembly is made larger. If, however, the specific heat becomes "infinite", large *fluctuations*, e.g. of density, become possible in regions of macroscopic size, though it is still sensible to talk about the *mean* density of the assembly. It can, for example, readily be shown that the specific heat is *proportional* to the *fluctuation* in the mean square energy (p. 49). In other words, a liquid near its critical point is "only just" stable, or, in Tisza's words, "the formalism of thermodynamics is strained to its limit" in describing such an assembly, just *because* the fluctuations are becoming large. The experimental data are consistent with all three of the quantities $(\partial^2 g/\partial P^2)_T$, $(\partial^2 g/\partial T^2)_P$, $(\partial^2 g/\partial P \partial T)$ approaching "infinite" values as we approach the critical point of a liquid, and we shall now examine, from another poiut of view, the question of the "stability" of such an assembly.

2.4. The Stability of a Phase near a Transition Point

We know from thermodynamics that an assembly can be described by means of a number of different thermodynamic potentials, and we shall now examine the behaviour of e, the internal energy per unit mass, as we approach the critical region of a liquid. The appropriate variables are v and s, the volume and entropy per unit mass. We have $P=-(\partial e/\partial v)_s$, $T=(\partial e/\partial s)_v$ so that, postponing for a moment the question of the validity of the process, we may make a Taylor expansion of e, as a function of s and v.

$$e=e_0+\mathrm{d}v\left(\frac{\partial e}{\partial v}\right)_s+\mathrm{d}s\left(\frac{\partial e}{\partial s}\right)_v+\frac{(\mathrm{d}v)^2}{2}\left(\frac{\partial^2 e}{\partial v^2}\right)_s+\frac{(\mathrm{d}s)^2}{2}\left(\frac{\partial^2 e}{\partial s^2}\right)_v+\mathrm{d}v\mathrm{d}s\left(\frac{\partial^2 e}{\partial v\partial s}\right)$$

Substituting for $(\partial e/\partial v)_s$ and $(\partial e/\partial s)_v$ we conclude that, as the critical point is approached, all three second differential coefficients of e approach the value *zero*, so that there is, as yet, no reason to doubt the validity of this Taylor expansion. By making use of the relation $g=e+Pv-Ts$, so that we have

$$\left(\frac{\partial g}{\partial v}\right)_{P,T,s}=\left(\frac{\partial e}{\partial v}\right)_P+P \quad \text{and} \quad \left(\frac{\partial g}{\partial s}\right)_{P,T,v}=\left(\frac{\partial e}{\partial s}\right)_P-T$$

we conclude, quite generally, that,

$$(\partial g/\partial s)_{v,P,T}=0, \qquad (\partial g/\partial v)_{s,P,T}=0 \tag{12}$$

which means that, at given values of P and T, the equilibrium values of v and s can be determined *either* by the equations $(\partial e/\partial s)_v=T$, $(\partial e/\partial v)_s=-P$, *or* by the exactly equivalent conditions (12) that g, considered as a function of v and s, takes a stationary value for fixed P and T. The *equilibrium* value of g is a function of P and T only, but, if e is known as a function of v and s, the variation of g with these quantities is known also. The second differential coefficients of e or g with respect to v and s then determine whether this stationary value is a maximum or minimum. We have

$$\left.\begin{aligned}&\left(\frac{\partial^2 g}{\partial s^2}\right)_{v,P,T}=\left(\frac{\partial^2 e}{\partial s^2}\right)_v=\left(\frac{\partial T}{\partial s}\right)_v=\frac{T}{c_v}\\ &\text{which is essentially positive,}\\ &\left(\frac{\partial^2 g}{\partial v^2}\right)_{s,P,T}=\left(\frac{\partial^2 e}{\partial v^2}\right)_s=-\left(\frac{\partial P}{\partial v}\right)_s\\ &\text{which is essentially positive in any physical assembly,}\\ &\left(\frac{\partial^2 g}{\partial v\partial s}\right)_{P,T}=\left(\frac{\partial^2 e}{\partial v\partial s}\right)=\left(\frac{\partial T}{\partial v}\right)_s\end{aligned}\right\} \tag{13}$$

which is positive for a gas or liquid near its critical point, but can be negative if the coefficient of expansion is negative. Thus, for a liquid, all three second differential coefficients of g approach zero from above, in whatever way we approach the critical point. Now, for equilibrium, it is necessary that g, considered as a function of s and v at a given P and T, shall always be a minimum, not a maximum. Expressed in another way, the quadratic form

$$\left(\frac{\partial^2 g}{\partial v^2}\right)_s(\mathrm{d}v)^2+\left(\frac{\partial^2 g}{\partial s^2}\right)_v(\mathrm{d}s)^2+2\left(\frac{\partial^2 g}{\partial s\partial v}\right)\mathrm{d}s\mathrm{d}v \quad (P \text{ and } T \text{ constant}) \tag{14}$$

must be positive definite. (This takes the place of the condition that, for a single independent variable, the second differential coefficient is positive at a minimum.) An assembly for which this form was negative definite or indefinite would not be physically realisable, because it would then be possible to find infinitesimal variations of v and s, related in such a way that g would decrease, and the assembly would, therefore, not be stable against small fluctuations, but would either break up into two phases or else would attain other values of v and s that *do* correspond to g being a true minimum.

We are thus led to think of the critical point as one at which the form (14) is "only just" positive definite. Now, as Tisza (1949) points out, it is *not* necessary that the limit of stability should be marked by the vanishing of all three second differential coefficients. The condition that (14) should be positive definite is

$$\begin{vmatrix} \frac{\partial^2 g}{\partial v^2} & \frac{\partial^2 g}{\partial v \partial s} \\ \frac{\partial^2 g}{\partial v \partial s} & \frac{\partial^2 g}{\partial s^2} \end{vmatrix} > 0 \quad (P \text{ and } T \text{ fixed})$$

a transition point being characterised by the vanishing of this determinant. It is obvious that this occurs if all four of the elements vanish, but that this is not by any means the only possibility. For example, we should equally well get a transition point if $(\partial^2 g/\partial s^2)_v$ remained finite, and the other two second differential coefficients vanished together, and it would be possible, in principle, to have a transition point at which all three of the coefficients remained finite, the determinant vanishing.

2.5. Cases where many Thermodynamic Variables are involved

Tisza extends this work to any number of thermodynamic variables, e.g. we need at least three pairs of conjugate variables to describe a magnetic material fully, even if there is no anisotropy. The vanishing of the determinant whose elements are the second differential coefficients of either the internal energy or the "magnetic Gibbs function" with respect to the "volume" variables (v, s, $B/4\pi$, etc.) again means that the phase we are studying is "only just" stable. If we use the notation x_i to represent one of the "volume" variables and P_i to represent the corresponding intensive or "force" variable ($-P$, T, H, etc.), we have, for any assembly, by the fundamental equation of thermodynamics (change of internal energy = heat supplied less external work done),

$$\begin{aligned} \mathrm{d}E &= T\mathrm{d}S - P\mathrm{d}V + H\mathrm{d}B/4\pi \\ &= \sum_i P_i \mathrm{d}x_i \end{aligned} \qquad (15)$$

so that

$$P_i=\left(\frac{\partial E}{\partial x_i}\right)_{x_j\ldots} \quad (j\neq i)$$

and therefore

$$\mathrm{d}P_i=\sum_k E_{ik}\mathrm{d}x_k \quad (i=k \text{ permissible}) \tag{16}$$

where

$$E_{ik}=\frac{\partial^2 E}{\partial x_i \partial x_k}$$

Provided that $D=\det((E_{ik}))$ does not vanish, we may invert the set of equations (16) to give us

$$\mathrm{d}x_i=\sum_k v_{ik}\mathrm{d}P_k \quad (i=k \text{ permissible})$$

so that

$$v_{ik}=\left(\frac{\partial x_i}{\partial P_k}\right)_{P_l\ldots}$$

and we have also

$$+v_{ik}=\frac{U_{ik}}{D} \tag{17}$$

where U_{ik} is the co-factor of E_{ik} in the matrix $((E_{ik}))$.

Now, by an extension of the work in two variables, D must be positive (the case $D=0$ marking a *limit of stability* and therefore corresponding to a transition point). Equation (17) shows us that then, in general, all the differential coefficients $\partial x_i/\partial P_k$ may be expected to be "infinite" at such a transition point, but that it *may* happen that some of them remain finite because of the vanishing of some of the corresponding co-factors U_{ik}, as well as, of D, at the transition temperature. One can foresee the possibility of a definite transition taking place without the appearance of a "λ point" type of specific heat anomaly, if $(\partial s/\partial T)$ remains finite at the transition point. Tisza (1949; 1951) suggested that the ferroelectric transitions of Rochelle salt and of barium titanate may really be of this type, but barium titanate has since been found to show a small latent heat at its transition, the spontaneous polarisation jumping to a finite value.

Such a "thermally induced" instability is obviously possible in principle, for example the elastic constants of a crystal might change progressively with temperature until one structure became unstable and was replaced by another, and this need not necessarily involve any significant alteration in the entropy. Such a hypothetical transition would be analogous to a framework under stress, which became unstable on heating because of alterations in the elastic properties of the material. See various articles in *Phase Transformations in Solids* (1951).

On the other hand, this behaviour must be regarded as "accidental", because analytically it requires the simultaneous vanishing of D and one or more of its minors. The critical point of a liquid seems to be "normal" in the sense that it only involves the vanishing of D itself, and the experimental evidence indicates that *all three* of the differential coefficients of the type $(\partial x_i/\partial P_k)$, i.e. $(\partial v/\partial P)_T$, $(\partial v/\partial T)_P$ or $-(\partial s/\partial P)_T$ and $(\partial s/\partial T)_P$ or c_p/T, are becoming "infinite", as the critical point is approached.

2.6. The possible Occurrence of "Stop-points"

It will be seen, therefore, that there are a large number of possibilities that are not foreseen at all by Ehrenfest's treatment. There is still another possibility to be considered, namely that, in the neighbourhood of the transition point, the Taylor expansion of g becomes impossible for some other reason than the occurrence of "infinities" in its differential coefficients. Thus, Zimm (1951) has very recently suggested that the critical point of a liquid may really be a "stop" at which not only the first two, but all the differential coefficients of v with respect to p vanish. (Similar behaviour is shown by, for example, the function $y=e^{-1/x}$ at the origin, and a Taylor expansion of such a function is impossible in any region that includes the origin.)

As we shall see below, many attempted theories of transitions which do not involve latent heat do predict a second-order transition of Ehrenfest's type, for example the Weiss theory of ferromagnetism (p. 115) and a number of theories of the order-disorder transition in alloys (p. 118). However, with the one exception of the superconductive transition already referred to (p. 11) where one has good reason to believe in the existence of an actual discontinuity in the specific heat, it seems equally possible to describe the facts in terms of Tisza's scheme outlined above. Nearly always there is evidence of a "tail" to the specific curve, and it is at least as easy to interpret the facts in terms of an "infinity" in the specific heat as it is in terms of a finite discontinuity. Onsager (1944) has shown that a simple physical model (two-dimensional lattice with interactions between nearest neighbours only) does, when worked out properly, lead to an infinity in the specific heat of just the kind ordinarily observed—the specific heat being "infinite" at the one point $T=T_0$ but continuous everywhere else.

2.7. Effect of altering the External Constraints

It seems advisable to point out that it has no meaning to specify the "order" of a phase transition, or to try to fit it into the more extended classification that we have suggested in this chapter, until we have specified the thermodynamic conditions under which we work. It is elementary that a quantity such as the specific heat is not defined unless

the precise thermodynamic conditions under which it is measured are stated. If the specific heat shows some kind of anomaly, under one set of conditions, it can happen that, under a slightly different set, it will become continuous, or have an anomaly of a different type. For example, consider the thermodynamic formula for the difference of the specific heats:

$$c_p - c_v = T\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P \tag{18}$$

Now, we know, experimentally, that both $(\partial v/\partial T)_P$ and $(\partial v/\partial P)_T$ for a gas become "infinite" at the critical temperature and pressure, and it would therefore be entirely possible, for example, for c_p to have an "infinity" at the critical temperature while c_v remained finite and continuous. See, for example, A. W. Lawson (1940).

As another example, consider an assembly consisting of liquid and vapour sealed up in a tube, the total volume of which is constant, and to which heat is applied. For simplicity, we suppose the latent heat per unit mass l, and the constant volume heat capacities per unit mass of the two phases, c_1 and c_2 to be independent of pressure and temperature. We neglect the compressibility and coefficient of expansion of the liquid and suppose that the vapour obeys the perfect gas laws. We suppose the masses of the two phases initially present to be m_1 and m_2 and suppose that a rise in temperature $\mathrm{d}T$ of the whole assembly leads to a mass $\mathrm{d}m$ of the liquid evaporating, and to the pressure increasing from P to $P+\mathrm{d}P$. The density of the liquid is supposed to have the constant value ρ_1, while the density of the vapour changes from ρ_2 to $\rho_2+\mathrm{d}\rho_2$. Then we have the following four equations:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{l}{T(1/\rho_2 - 1/\rho_1)} \tag{19}$$

(the Clausius-Clapeyron equation)

$$\frac{\mathrm{d}\rho_2}{\rho_2} = \frac{\mathrm{d}P}{P} - \frac{\mathrm{d}T}{T} \tag{20}$$

(from the gas laws),

$$\mathrm{d}q = l\mathrm{d}m + m_1 c_1 \mathrm{d}T + m_2 c_2 \mathrm{d}T \tag{21}$$

(by conservation of energy), and

$$0 = \mathrm{d}\left(\frac{m_1}{\rho_1} + \frac{m_2}{\rho_2}\right) = -\frac{\mathrm{d}m}{\rho_1} + \frac{\mathrm{d}m}{\rho_2} - \frac{m_2 \mathrm{d}\rho_2}{{\rho_2}^2} \tag{22}$$

since the total volume is constant.

Equation (21) is a simple consequence of the conservation of energy. No work is done on or by the assembly since its total volume is constant

and the work done by the two phases due to the motion of the interface cancels out. c_1 and c_2 can then be taken as the heat capacities per unit mass at constant volume and, for simplicity, we suppose that they are both independent of pressure. We also suppose that the mass of liquid m, is such that it has completely evaporated before the critical point is reached. Then, from equation (21), we have

$$\frac{\mathrm{d}q}{\mathrm{d}T}=\frac{l}{\rho_2}\frac{m_2}{1/\rho_2-1/\rho_1}\left(\frac{l}{PT(1/\rho_2-1/\rho_1)}-\frac{1}{T}\right)+m_1c_1+m_2c_2 \qquad (23)$$

where $\mathrm{d}m$ can be obtained from equations (19), (20) and (22) by eliminating $\mathrm{d}\rho_2$ and $\mathrm{d}P$ between them, and this quantity is easily shown to be finite and positive and independent of m_2. Equation (23) then shows that, just below the temperature at which m_1 is zero, the heat capacity per unit mass present in the tube is

$$c_2+\frac{l}{(1-\rho_2/\rho_1)}\left(\frac{l}{PT(1/\rho_2-1/\rho_1)}-\frac{1}{T}\right)$$

whereas, just above this temperature, vaporisation has ceased and the heat capacity per unit mass is just c_2. Thus, supposing we had a substance whose heat capacities per unit mass, c_1 and c_2, were equal in liquid and vapour, we should nevertheless observe an apparent discontinuity in the heat capacity if we measured it under these special conditions. Thus, by altering the quantities that are held constant, it is readily seen that the nature of a specific heat anomaly may be completely changed. Thus, in a ferroelectric, considerable care has to be taken to specify exactly what is being held constant. See p. 230.

We have emphasised this point by giving specific examples of it, because it sometimes happens that what appears to be mathematically the same model can predict widely different types of phase change when applied to different physical problems. Consider, as an example, the Weiss model of a ferromagnetic (p. 115) which amounts to introducing an interaction between elementary systems independent of their distance apart. This model is known to have a transition temperature T_c, and by appropriate transcriptions of the physical variables, keeping the mathematical form of the interaction term the same, the model can be made to give rough theories of a number of co-operative phenomena. We list a few below, indicating the type of thermodynamic constraint that is imposed in each case. To avoid confusion, we describe the model always in magnetic terms, on the understanding that, when the model is applied to other types of problem, the appropriate transcription of variables is to be made. For example, in the order-disorder problem $I/N\mu$ must be replaced by S, the degree of order. The classification of the anomalies into types follows the notation of Section 2.3 above.

TABLE I

Phenomenon	*Type of Constraint*		*Type of Anomaly*
Ferromagnetism	$H=0$ and constant	B_1	Second order at $T=T_c$
,,	$H\neq 0$ and constant		None
Order-disorder in 50 per cent alloy	$H=0$ and constant	B_1	Second order at $T=T$
Critical adsorption	$T<T_c$ and constant	A	First order at $H=0$
Liquefaction of imperfect gas	$T=T_c$ and constant	C_3	λ-point at $H=0$
,, ,,	$T<T_c$ and constant	A	First order at $H=0$

Details of the transcriptions necessary to go from the ferromagnetic to the order-disorder or critical adsorption problems are given on p. 129, while the transcriptions necessary to relate the liquefaction problem to the ferromagnetic one are given by Temperley (1954).

2.8. Nomenclature

The expression "second-order transition" often causes confusion because it has acquired several meanings. It is often used to convey the simple idea that a transition is devoid of latent heat, or to describe one or both of the situations corresponding to transitions of types B or C above. The author suggests that the expressions Curie-point or lambda-point should be used to convey the idea of absence of latent heat and that, when it is also necessary to distinguish between types B and C, this can be done very simply by introducing the names of Ehrenfest and Tisza respectively. A further source of confusion is that some writers use the term "second order transition" to describe the rapid rise in the specific heat of a glass that often occurs over a small temperature range, and a very similar phenomenon that occurs in polymers, often associated with the transition from a brittle to a "plastic" or "rubber-like" texture. Properly speaking, this is not a true phase-transition at all, but the rapid rise in specific heat is associated with the "thawing-out" of a particular degree of freedom, its associated time-constant changing from a large to a small value in the manner discussed below in Chapter 3 (p. 33), as the result of the presence of an activation factor of the type exp (U/kT).

In a long-chain polymer, the degree of freedom in question is almost certainly the possibility of the occurrence of "kinks" in the hydrocarbon chain. See Temperley (1956) for a discussion. Below the glass-like transition region, the chain can be considered to be "stiff at the joints" and the polymer behaves like an ordinary solid, while above this region, the mutual orientations of neighbouring carbon-carbon valencies will change fairly frequently, and the effective appearance of this extra degree of freedom calls for a corresponding extra factor in the partition function, leading to a larger specific heat, while the flexibility leads to the appearance of rubber-like properties. However, it is never possible to associate a definite transition *temperature* with this effect, since there

is no temperature at which the "brittle" and "rubber-like" states are in equilibrium; the appearance of rubber-like properties is gradual.

Again, if we heat common glass or plastic sulphur, we pass continuously from a rigid solid to a supercooled liquid, but the change in viscosity with temperature is quite continuous. The distinction between the two is a matter of definition and the result of a specific heat measurement shows a noticeable dependence on the rate at which heat is supplied. Here again, it is hardly possible to speak consistently of a phase transition.

The *devitrification* of glass, however, corresponds to the formation of a *crystalline* phase, distinct from the usual *amorphous* state of solid glass, and this must be reckoned to be a true phase transition. Although the equilibrium melting temperature may be hard to measure experimentally, it undoubtedly exists, and could, in principle, be located if enough time were allowed for the liquid and crystalline phases to come into proper equilibrium.

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CHAPTER III

Some General Theoretical Considerations

3.1. What does one ask of a Theory of a Change of State?

In the last chapter we have shown that preliminary insight into the nature of a change of state may be obtained by a thermodynamic analysis of the data. We must now inquire what further information we may hope for from any detailed theory of a change of state that may be developed. We have already pointed out that the resources of statistical mechanics are not yet such as to enable us to deduce the rigorous consequences of *any* realistic molecular interaction function. We might, therefore, ask two things about a new theory of a change of state:

(a) Does it give a satisfying physical picture of what is probably happening?

(b) Is the numerical agreement with the observed facts in keeping with the number of adjustable parameters, or is the theory unduly "forced" in this respect?

The answer to either of these questions usually has to be a matter of opinion. One cannot simply say that theory A is "better" than theory B "because it is in closer agreement with observed facts", if this improved agreement has been obtained at the expense of introducing one or more extra parameters. One might perhaps inquire whether, "other things being equal", a one-parameter theory that agrees with the facts within 10 per cent is *a priori* more or less likely to be correct than a three-parameter one that agrees with the facts within 0·1 per cent, but, as far as the author knows, this exercise in probability theory has never been seriously attempted, and one must consider each case separately on physical grounds.

3.2. The Notion of a Co-operative Change

It is not obvious *a priori* how a sudden change in the properties of an assembly at a particular temperature can be predicted by statistical mechanics at all. For we know, from the general theory of statistical mechanics, that all the thermodynamic properties of an assembly follow if we can calculate the partition function

$$f=\sum_r g(r)\mathrm{e}^{-E_r/kT}$$

where $g(r)$ is the number of physically distinct ways in which the assembly can assume a complexion of energy E_r. Now, it can be shown without difficulty that, for an assembly containing a finite number of molecules f should be differentiable any number of times with respect to T, so there should be no singularity at any temperature, since the function $e^{-E_r/kT}$, representing the Boltzmann factor associated with the level of energy E_r, varies quite smoothly with temperature, and the observed thermodynamic quantities, such as heat content, pressure, etc., represent various *averages* of this quantity taken over all the levels, so it is not easy to see how any of them can vary abruptly.

This paradox is resolved when we recognise that we get a true mathematical discontinuity only in the limiting case of a very large assembly in which case infinitely many terms contribute effectively to the series for f, and it, or some of its derivatives, may *fail to converge* for some value of the temperature. The corresponding sharp, but not mathematically discontinuous, changes predicted by theory for a large but finite assembly (containing perhaps 10^{22} molecules) are, from an experimental point of view, indistinguishable from those that would be expected for an "infinite" assembly, and it is always in this sense that we speak of "infinite" specific heats, etc. We might therefore expect theories of transition points to consist of a study of the relationship between $g(r)$ and E_r in the limit when the number of molecules becomes very large. In thermodynamic terms, this can be expressed as the relationship between the entropy and the energy.

Thus, suppose that we are studying an assembly at a fixed volume and temperature. The condition of equilibrium is that the free energy $F=E-TS$ is a minimum. For T very small, this means that the energy E will take as low a value as possible, for T very large, the equilibrium state will be the one for which S, the entropy, is a maximum—that is the state which can be realised in the greatest number of ways. The relative importance of the two terms in F obviously changes with T, and the change over from a state of low energy to a state of high entropy may go quite smoothly with temperature, or with various degrees of abruptness, depending on the precise relationship between E and S.

It is actually true that any theory of a change of state can be exhibited in this way, but, before discussing this, we may mention an alternative point of view, which, although not quite so general, has been the basis of nearly all theories of changes of state until very recently. We may suppose that we possess the solution of a problem such as that of the perfect gas. This shows no critical behaviour, because the interactions between molecules are neglected. We may attempt, as did van der Waals, to take these interactions into account by adding a correcting term to the pressure to allow for the attractions of the molecules, and subtracting a correcting term from the volume to allow for the fact that

the molecules are of finite size. As is well known, the equation of state then runs

$$(P+a/v^2)(v-b)=RT \qquad (1)$$

We postpone the detailed discussion of this and similar equations to a later chapter. For the present, we need only the well-known fact that equation (1) is not an explicit equation determining v as a function of P and T, but is an implicit equation which may have as many as three real roots. This circumstance arises from the presence of the term a/v^2 *which itself depends on the volume* v. If we had merely added a constant term to the pressure in an attempt to correct for the attractions, we should have got nothing very remarkable, but a term like a/v^2 itself increases in importance as the volume decreases, so that, if we steadily reduce the temperature, it eventually becomes thermodynamically advantageous for the assembly to contract sharply in volume, the entropy loss associated with this having to be set against the gain in energy due to the work done by the attractive forces. Thus, the presence of the term a/v^2 has led to a real "landslide" at a definite temperature. It was this circumstance that led Fowler to introduce the name "co-operative transition", which emphasises that the interaction must be "self-helping" in the sense of increasing in importance with the progress of the change it is tending to promote. Closely connected with this is the idea that such transitions cannot be understood in terms of the properties of individual atoms and molecules but only if we make some attempt to take account of their interactions, which is normally done by means of terms like a/v^2.

3.3. Relation between Type of Transition and Nature of Interaction

As is well known, the van der Waals equation leads to condensation—that is to a discontinuous change in volume associated with a latent heat, that is to a typical first-order transition. We now ask *what types of interaction function are associated with the various possible types of transition* considered in Chapter II. The answer to this question is imperfectly known, and is probably very complicated, but it does seem possible to make the following generalisations on a provisional basis.

(a) If the interaction is of "long-range" type, it will probably lead to either a first-order transition, or else to a second-order one of Ehrenfest's type. (Type B, 1 or 2 in Chapter II.)

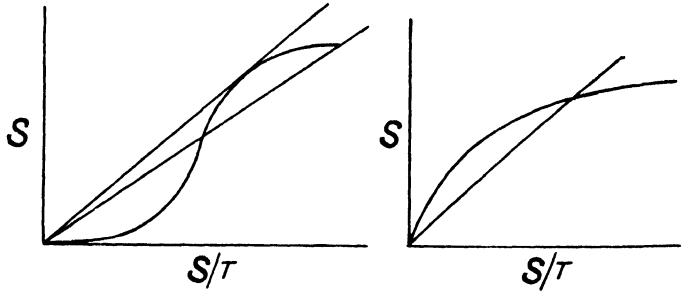
(b) If the interaction is of "short-range" type, it will probably lead to a transition in which one or more of the second derivatives of the appropriate thermodynamic potential become "infinite" or zero. (Type C, Chapter II.)

These state a good deal more than is actually known—statement (a) has only been formally proved for the extreme case in which the interactions do not fall off with distance at all, while statement (b) has only been established for certain models in which all interactions except those between nearest neighbours are neglected. We are therefore not, at present, in a position to say what is the distinction and where is the dividing line between "long-range" and "short-range" interaction in this sense (points that writers, using these terms in other contexts, often fail to make clear). Also, the possibility that a model with an interaction that falls off smoothly with distance may exhibit other types of behaviour, distinct from both (a) and (b), cannot be excluded.

As an illustration, we may consider the behaviour of the Bragg-Williams (1934) model of order-disorder in an alloy. The assumed variation of the configurational energy, E, with the "degree of order", S, $E=1/2W_0(1-S)$ can be shown to be equivalent to the assumption of an interaction of *infinitely long range*. S, the degree of order, is defined in such a way as to be zero for a random arrangement, unity for a perfect superlattice. The variation of S with temperature has to be determined by solving the equation

$$S=r(1-r)(1-S)^2(e^y-1) \qquad (2)$$

where $y=SW_0/Nr(1-2)kT$



(a) (b)

Fig. 2. Determination of equilibrium degree of order.

The numbers of atoms of the two types are given by $N_A=Nr$, $N_B=N(1-r)$. If we plot the right-hand side of (2) as a function of S we get a re-entrant curve (fig. 2 (a)), and apart from the root S=0 (complete disorder) which always satisfies (2), there is a non-zero root below a certain temperature T_m. However, the existence of such a root does not yet mean that the ordered state, S finite, is the most stable one, and further investigation shows that the change over occurs when the line

$$y=\frac{SW_0}{Nr(1-r)kT}$$

cuts off equal areas from the curve

$$y=\log\left\{1+\frac{S}{r(1-r)(1-S)^2}\right\}$$

The behaviour of the free energy as a function of S is shown schematically in fig. 3 (a) from which it will be evident that, at the critical temperature, a finite jump occurs in S, accompanied by a finite change in internal energy, that is a latent heat. If, however, $r=\frac{1}{2}$, i.e. if equal numbers of the two kinds of atom are present, the re-entrant part of the curve in equation (2) disappears, and we have instead to solve the implicit equation (fig. 2 (b))

$$S=\tanh\left(\frac{SW_0}{NkT}\right) \tag{3}$$

According to this equation, which is mathematically the same as that occurring in one form of the Weiss theory of ferromagnetism, non-zero values of S are possible only for T below W_0/Nk. The non-zero root is then, when it exists, always the more stable, but we now have it *coinciding with the zero one* at $T=T_0$ and *gradually growing* as the temperature drops below this. The corresponding behaviour of the free energy is shown in fig. 3 (b). This time there is no latent heat, and the model turns out to have a transition of the second order of Ehrenfest's type. Unfortunately there are, at present, insufficient data available to enable us to draw diagrams analagous to 3 (a) or 3 (b) for a model with very short-range interaction. (The approximate treatments such as those of Bethe (1935) and Kirkwood (1938) are insufficiently accurate for this purpose.)

3.4. First-order Transitions. Stable and Metastable Equilibrium

Reference to fig. 3 (a) shows the typical behaviour of the free-energy curve when we approach a first-order transition. We must remember that only minima in the free-energy curve represent physically realisable states (points such as X and Y in fig. 3 (a)), and if, by a fluctuation, the assembly is brought into a state with a free energy appreciably different from one of these minima, there is a very strong tendency for the free energy to approach the minimum value again. This can easily be deduced, either from the thermodynamic principle of increase of entropy (Roberts and Miller (1951), *Heat and Thermodynamics*) or as a consequence of statistical mechanics (that is, from probability theory) (Fowler (1936), *Statistical Mechanics*, Chap. II).

Now, if an assembly were initially at a point such as Y (fig. 3 (a)) it could, in principle, remain in the corresponding thermodynamic state indefinitely, in spite of the fact that a state such as X is of a lower free

energy. This arises from the fact that a large fluctuation is needed to carry the assembly from Y to X over a "hump" in the free energy such as that at Z. The assembly could be "carried over the hump" by a random fluctuation of sufficient size, or by the formation of a *nucleus* of the more stable phase. Of these, the formation of a *nucleus* is by far the more probable mechanism, the probability that a random fluctuation of the whole assembly should lead to a significant increase in its free energy being very small when the assembly is large. On the other hand, the formation of a nucleus may not be easy even if it contains only a small number of atoms. Indeed, if it *were* easy, one would expect nuclei of different sizes to form under slightly different external conditions, and thus a tendency to *smooth out* the sharpness of the transition would become noticeable. In this case the transition would probably not be recognised as a co-operative one at all.

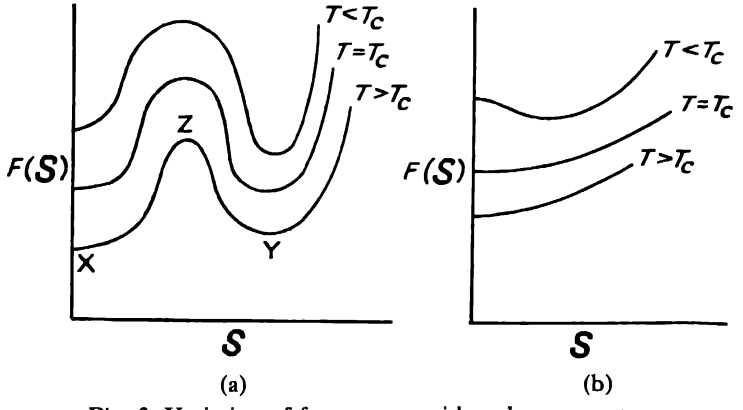


Fig. 3. Variation of free energy with order parameter.

It must be remembered that the formation of a nucleus implies not only the creation of a region of the other phase, but also the appearance of "regions of misfit" which necessarily occur between two different phases. If the nucleus is small, the free energy associated with the regions of misfit may dominate the situation, as it will be proportional to the area of the *surface* of separation and may well become comparable with the "free energy of transition", proportional to the *volume*. Among cases that have been studied in detail are the superheating of liquids and supercooling of vapours. Here the formation of a nucleus is hindered by "surface tension" (pp. 89–94) with the result that supercooled vapour, superheated liquid, or liquid under tension, can exist for very long periods. Another case which involves "regions of misfit", though strictly speaking, it is not a phase transition, is the reversal of the direction of magnetisation of a ferromagnetic domain (p. 208). Here, it turns out that energy is needed to create the "regions of misfit" between two

domains, because these regions are of finite thickness. They are usually described as "domain walls". A third such transition is that between superconducting and normal metal, where it also seems likely that there is a "surface tension" between the two phases, and the existence of an "intermediate state" consisting of a mixture of the two phases, has been experimentally proved (pp. 267–76).

The phenomena associated with these three types of nucleation will be described in detail later on, meanwhile we have the general picture that a nucleus may be prevented from expanding, or even from forming at all, by surface effects. In this case the metastable phase could, ideally, persist until conditions are changed so much that the free energy "hump" YZX (fig. 3 (a)) drops to nearly zero, at which stage only a very small fluctuation is sufficient to promote the transition. This situation can be illustrated in a rather more familiar fashion if we consider the van der Waals imperfect gas. Fig. 4 shows some typical isothermals, and, while the most stable states of such an assembly are represented by isothermals such as the parts of the curve DE and IJ,

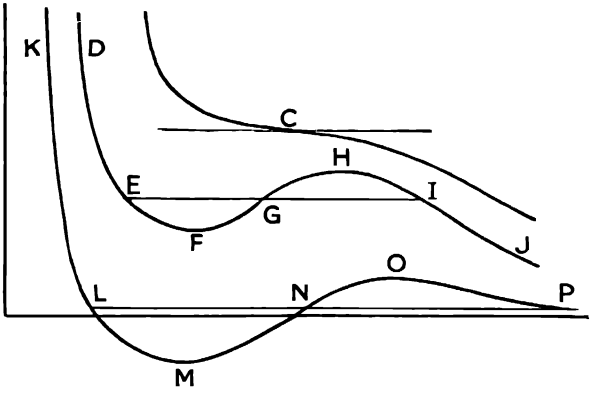


Fig. 4. Isothermals of van der Waals gas.

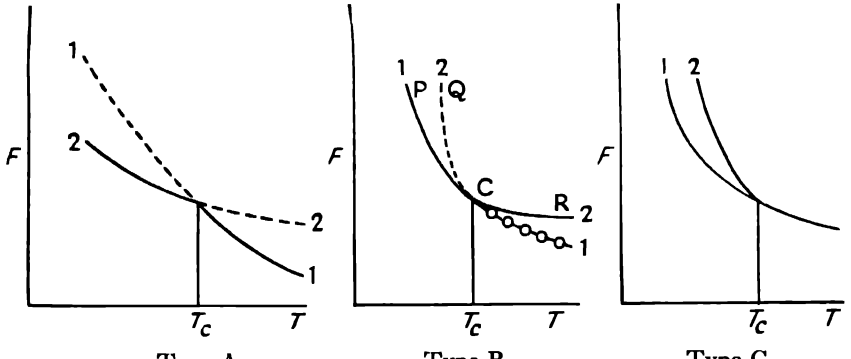
together with the line EGI representing the two-phase region, it is nevertheless possible to realise regions such as EF, HI, LM and PO, which correspond to *local*, but not absolute, minima of the Gibbs function g (considered as a function of v at fixed pressure and temperature). On the other hand, regions such as FGII are found to correspond to *maxima* of g, so are analogous to points such as Z in fig. 3 (a), and, can, therefore, in no circumstances be physically realisable.

3.5. Conditions that must be satisfied for a Transition of Ehrenfest Type to be possible

This is the general situation when we have a transition of the first order involving a latent heat, and corresponding finite jumps in one or

more of the parameters such as the density and entropy specifying the assembly. When, however, the latent heat vanishes, the situation shown in fig. 3 (a) is no longer possible. Instead, we must have some such situation as that shown in fig. 3 (b), in which a single minimum in the free energy splits into two, which gradually move further apart as the temperature is lowered. Thus, the two phases are not distinguishable until we are actually below the transition temperature, T_c, and we cannot think, as we can in fig. 3 (a), of two physically distinguishable phases in equilibrium at the transition temperature. As an example, behaviour of the type shown in fig. 3 (b) occurs with the Weiss model of ferromagnetism, spontaneously magnetised domains appearing below the transition temperature, but the spontaneous magnetisation is actually zero at the transition temperature so that the magnetised and unmagnetised phases are then identical. Similar behaviour probably occurs near the critical point of a liquid, the two phases becoming more and more unlike as we go below the critical temperature, but the precise details of the behaviour are still uncertain. See Chapter IV.

We may look at the situations shown in figs. 3 (a) and (b) from a slightly different angle. Imagine curves (a) placed in front of one another to form a "solid graph" of F, as a function of S the degree of order and T. In fig. 5 (a) we plot, as functions of T, the position of the minima of F, which alone correspond to possible equilibrium states, the lines 1 and 2 corresponding to the two sets of minima. The full portion of each curve corresponds to the lower minimum of F, and therefore to the more stable phase. It will be seen that the curves cut at a certain temperature, that at which the two phases are equally stable, and that there is a discontinuity in $(\partial F/\partial T)_V$, that is in the entropy, so that such a transition involves a latent heat. The dotted portions of the two curves represent metastable phases, and there is a free energy barrier between the metastable and the stable phase everywhere except at the transition temperature itself where both phases are equally stable. Fig. 5 (b) represents a



Type A Type B Type C

Fig. 5. Behaviour of the free energy for various types of transition.

similar plot of the minima of F for a phase-change such as that shown in fig. 3 (b). Here there is no latent heat at the transition, which means that the entropy must be the same for both phases. This means that the two curves of minima of F must not merely cut, but touch, so that both F and $(\partial F/\partial T)_V$ are the same. This entails one of the curves (2 say) lying entirely above the other, which would seem to mean that phase 1 is always the more stable, in which case it would be without physical meaning to postulate the existence of phase 2 at all. This difficulty can be avoided in two ways:

A. We may postulate that the contact between the two curves involves *three* points in common (contact of the second order) so that the curves cross at their common point. This would imply a transition of the *third* order, in Ehrenfest's classification, $(\partial^2 F/\partial T^2)_V$ or the specific heat, being the same for both phases as well as F and $(\partial F/\partial T)$.

B. We may postulate that, for some mathematical or physical reason, the part of the curve shown with circled points fig. 5 (b) cannot exist, so that phase 2 is then the only realisable one above T_c, while both phase 1 and 2 can exist below it. On the Weiss model of ferromagnetism, one of the curves of free energy comes to a "natural end" at the transition temperature. This happens because the spontaneous magnetisation is zero there and we do not distinguish between positive and negative spontaneous magnetisation. Thus, if the curve QCR (fig. 5 (b)), corresponds to the unmagnetised state, and the curve PC to the magnetised one, the domain will be highly magnetised at P and unmagnetised at C. If we let the magnetisation become negative, the energy and entropy are, in the absence of a magnetic field, just the same as they are for an equal positive magnetisation, so that the curve PC represents *both* signs of magnetisation. Let us suppose that the magnetisation is slowly changed, I being initially positive, passing through the value zero and becoming negative. This corresponds to tracing out the curve from P to C and then back to P, so that C is in fact a "natural end" to the curve. A similar effect can occur in certain models of liquid helium II (p. 303) because the occupation number of an energy level cannot be less than zero, and it may happen that a "natural end" to a free energy curve arises in *this* way. Similarly, it might arise, in an assembly obeying Fermi statistics, through a set of levels becoming completely filled or completely empty. Thus a second-order transition of type B is not, as has been stated by some authors, *impossible* to realise, but it does require the existence of a parameter such as spontaneous magnetisation which has a limiting value which it cannot transgress, and it is also necessary that this parameter assumes this limiting value *at* the Curie temperature so that we *do* have extra conditions to satisfy, which would not be needed if the transition were of odd order.

Fig. 5 (c) is an attempt to represent the probable situation in a transition of type C, e.g. the critical point of a liquid. Here the two curves must touch as there is no latent heat. The "infinite" specific heat requires that the curves "roll themselves up" because $\partial^2 F/\partial T^2$ is "infinite" for both phases. It is also necessary that the curves do not again separate above the critical point, but are continued as a single curve. Near the critical temperature, the "free-energy barrier" between the two phases is very low, and accordingly there are large local fluctuations of density giving rise to opalescence (p. 50). We can thus safely conclude that transitions without latent heat demand more subtle considerations for their discussion than do first-order ones. It may well be that some of the supposed second-order transitions are really of type C, at least we do not at present know of a definite case of one of type B (1). The transition of liquid helium was long thought to be of this latter type, but very recent evidence, Atkins (1953), Atkins and Chase (1951), shows that it may equally well be of type C, the expansion coefficient and the compressibility perhaps even being "infinite" at the transition temperature instead of being *discontinuous*, while the experimental evidence on the specific heat is quite compatible with this being "infinite" also. The theory of liquid helium due to F. London (1939) gave a second-order transition of Ehrenfest type, Class B, type 1. Here the logical difficulty just discussed also does not arise because, according to the London theory, the lowest energy level of the assembly becomes practically empty at the transition temperature. Since we do not recognise the possibility of negative occupation numbers, there is no difficulty in imagining one of the free-energy curves coming to a "natural end", the circled points, fig. 5 (b), representing the values that one would deduce mathematically if we calculated the free energy from the partition friction, admitting the possibility of negative occupation numbers.

For the superconductive transition, type B (2), it is probable, but not certain, that certain electronic states become empty above the transition temperature, so that here also the theoretical difficulty probably does not arise; there is a "natural end" to one of the free-energy curves.

3.6. Irreversible Phenomena associated with Transitions

Many transitions are associated with irreversible effects, which can sometimes be removed by proper choice of the experimental conditions. While the phenomena are so diverse that each case has to be considered separately, it is possible to recognise a number of possible basic causes of irreversibility and to see why some of them become more and more difficult to remove as we approach the transition point. We first give a list of common effects:

A. We have already noticed that, in first-order changes, there is necessarily a "free-energy barrier" tending to prevent the phase-change taking place at the true transition temperature. This barrier completely prevents the whole assembly from making the transition together, but allows the change to proceed through the formation of one or more nuclei of the more stable phase. (This, however, may be prevented, or made difficult, by surface effects.)

B. It may happen that there is some intrinsically irreversible process brought into play by the transition, which cannot be removed without spoiling the effect studied. As an example of this we may mention the fact that the magnetisation of a ferromagnetic material cannot be changed without causing eddy-currents. Since the ferromagnetism itself is due to the "conduction" electrons, it is evident that we cannot completely "kill" the eddy-currents and yet keep the ferromagnetism. It is, however, possible to reduce their importance considerably by changing the applied fields sufficiently slowly, and by the familiar device of working with powdered specimens, though, as we shall see, there are other associated effects, leading to ferromagnetic *hysteresis*, which cannot be removed in this way.

C. It sometimes happens, for example in alloys with a superstructure, that the time-constant associated with the structural change becomes longer and longer as the transition temperature is approached. This reminds one of what happens in a mechanical system when instability is approaching. If x represents a possible displacement of the system, the condition for equilibrium, if V is the potential energy, is $\partial V/\partial x=0$ while the equilibrium is stable or unstable according as $\partial^2 V/\partial x^2$ is positive or negative. If $\partial^2 V/\partial x^2$ is positive but small, the system is "only just" stable, and the approaching instability shows itself by the period of oscillation becoming longer and longer. For the equation of motion for small oscillations is

$$\mu\frac{\mathrm{d}^2x}{\mathrm{d}t^2}+x\frac{\partial^2 V}{\partial x^2}=0 \qquad (4)$$

where μ is a quantity, of the dimensions of a mass, which depends on the geometry of the system. It is clear that the period of the oscillation becomes infinite if $\partial^2 V/\partial x^2$ is zero.

We know that the thermodynamic functions such as F, G, etc., possess many of the properties of potential energy, e.g. they take stationary values for equilibrium, the derivative of internal energy E with respect to an extensive quantity such as V or S gives the intensive quantity like P or T, which can be interpreted as a "generalised force". One might push the analogy further and argue that instability should be accompanied by a vanishing of some of the second derivatives of E and, as we have seen above (p. 12), this is sometimes, but not always, so. This analogy cannot be pushed too far, e.g. we do not know of any simple

statistical mechanical analogue of the "effective mass" μ, occurring in equation (4), in an assembly in which TS is comparable with E. However, the analogy is helpful, in that it makes the correct prediction that time constants should sometimes *become longer as we approach a transition point*, though the full explanation is certainly more complicated, see p. 41. In some cases, e.g. the ordering of alloys, this effect is very serious, because the time constants are nearly always of the order of minutes or hours, and any further lengthening makes observations difficult.

We consider briefly one definite reason why a transition can be masked or prevented in this way. Time-constants associated with processes such as the rearrangement of atoms in a crystal usually vary with temperature according to a factor like $A \exp(U/\boldsymbol{k}T)$, U being, for example, the energy barrier which two atoms that are attempting to change places in the lattice have to surmount. The presence of this factor is easily understood, the transition will not take place unless an atom has first obtained the energy U, the probability of which is proportional to $\exp(-U/\boldsymbol{k}T)$. A similar factor occurs in the time-constants of chemical reactions where it is known as the activation energy. (The calculation of the multiplying constant A can only be carried out in simple types of assembly, though it is often assumed to be of the order of $\boldsymbol{k}T/\boldsymbol{h}$.)

Now it may easily happen that the activation energy U is large compared with $\boldsymbol{k}$ times the transition temperature. For example, in the ordering of an alloy, it is necessary for two atoms to "squeeze past" their neighbours in order to exchange places, and this may be difficult because of the large repulsive fields between atoms. On the other hand, when the change has taken place the *final* loss or gain of energy, corresponding to the difference between the energies of a pair of like and a pair of unlike atoms, which determines the transition temperature, is quite small in comparison with U. Again, a molecule in a solid may have a dipole moment but any lining-up of the dipoles might involve turning round the whole of a large molecule into a new orientation, which might again involve a potential barrier much larger than the dipole-dipole interaction itself, in which case also $U/\boldsymbol{k}$ would be large compared with a possible transition temperature.

In this sort of situation it is possible for transitions to be hindered or suppressed because, by the time the assembly is cooled down to a temperature at which the transition could theoretically take place, there is no effective mechanism available by which it can do so, the appropriate time-constants have by now become long because of the factor $e^{U/\boldsymbol{k}T}$. The transition temperature times $\boldsymbol{k}$ is always comparable with the interaction energy (per atom) that is responsible for it, but if the activation energy U is large compared with this, the time-constant may have

become very long, and the attainment of the thermodynamically most favourable state may in practice be prevented. A familiar example of this sort of behaviour is the solidification of common glass. The theoretically most stable state is the crystalline one, but the vitreous or amorphous state is the one that is obtained by cooling at any ordinary rate. At room temperature, the time-constant for its conversion to the crystalline state seems to be of the order of years; most laboratory workers are familiar with "devitrification", the appearance of crystals in *old* glass that is heated slightly.

We have thus described three distinct types of situation in which the occurrence of an irreversible effect is so intimately connected with the mechanism of the transition itself that it is difficult to see how the transition could be carried out reversibly even in a completely "idealised" experiment. The problem is on a distinctly different plane from the ordinary processes of reasoning by which one justifies, for example, the conception of a Carnot cycle. It is permissible to think of "good conductors", "heat insulators" and "frictionless" processes because one can often approach these ideals very closely in practice. Even when one cannot do this, one can measure, for example, the frictional forces by separate experiments, which enables us to allow for their effects, but the situation is altogether different when one cannot make, even in theory, such "blank" experiments. Such will be the case in the examples just discussed.

3.6.1. "Irreversible Thermodynamics"

Our classification of changes of state into types (Chapter II) made use of reversible thermodynamics, and we have to consider how far thermodynamical arguments can be considered as valid if an irreversible change inevitably accompanies our transition. The customary procedure of replacing the equalities of reversible thermodynamics by inequalities would not help us in our attempts to classify transitions into types (though it might make it possible to draw some very superficial conclusions). Further, transition points are explained by the application of statistical mechanics to various types of model, but it is always assumed, at least implicitly, that one is dealing at all times with the true equilibrium state of an assembly. Strictly speaking, statistical mechanics has nothing to say about the *mechanism* by which an assembly *approaches* its equilibrium state, but implicitly assumes that a sufficiently rapid mechanism does exist. We are thus led to ask whether it is possible to generalise either thermodynamics or statistical mechanics to describe irreversible processes. These are the only alternatives to the attempt to develop an approach on the basis of kinetic theory.

Of recent years, many attempts have been made at such a generalisation of thermodynamics. Two approaches are possible, one may

attempt to "patch up" such results as Kelvin's celebrated but faulty derivation of the thermo-electric relations, and to use the "patched-up" theory for other cases, or one may attempt to reformulate statistical mechanics in a way that will enable a description of non-equilibrium states to be given. The conclusions can then be translated into thermodynamic language if desired. The direct "patching-up" of thermodynamics is most suitable for discussing assemblies in which the departure from equilibrium is small, such as a flowing gas in which viscosity is taken into account. The essential point here is that the hydrodynamic stream velocity is always small compared with the velocities of the molecules themselves, so that we may consider that setting the gas in motion results in only a slight departure from the equilibrium state. We may then take over the static definitions of entropy, although, strictly speaking, entropy can only be defined thermodynamically by reference to ideally reversible operations which are carried out very slowly. Our "irreversible thermodynamics" then consists of two assumptions—first that we can define "entropy content" as the same function of temperature and pressure as it is in a stationary gas, secondly that we can calculate the "creation of entropy" simply by computing, for example, the rate of doing work against viscosity and dividing by the temperature at each point. On this basis, we can derive an equation of entropy balance which, combined with the ordinary equations of hydrodynamics and the equation of state, is theoretically sufficient to enable us to determine the whole history of our system, starting from given initial conditions.

This approach must, however, fail in many cases that are of interest to us in discussing a change of state, where the entropy created as a result of the irreversible processes is not small. It would certainly fail in the flowing gas when the stream velocity became comparable with the velocity of thermal agitation, because we could then no longer define the entropy in the way just described, and we do not know how to generalise this definition further, nor, indeed, do we know in general whether we can give the concept of "entropy" any precise meaning in such conditions. We fail, for a somewhat different reason, if we attempt to improve on Kelvin's discussion of thermocouples, two of which are supposed to be connected by wires, and computations are made of the energy and entropy changes when unit charge is taken round the circuit. We reach correct conclusions if we simply neglect *all* irreversible effects, assuming as usual that the energy associated with them could be made as small as we please compared with the reversible Peltier heat by a proper choice of the conditions. This assumption is, however, a fallacy. A little consideration shows that we cannot at the same time make both the heat flow between the two junctions due to heat conduction, and the energy dissipated by Joule heating small compared

become very long, and the attainment of the thermodynamically most favourable state may in practice be prevented. A familiar example of this sort of behaviour is the solidification of common glass. The theoretically most stable state is the crystalline one, but the vitreous or amorphous state is the one that is obtained by cooling at any ordinary rate. At room temperature, the time-constant for its conversion to the crystalline state seems to be of the order of years; most laboratory workers are familiar with "devitrification", the appearance of crystals in *old* glass that is heated slightly.

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with the Peltier heat. By making the conductors short and thick, we can certainly reduce the Joule heat compared with the Peltier heat, but, at the same time, we shall increase the heat losses by conduction. We can only reduce these by making the wires long and thin, which increases the Joule heat. Thus, we cannot consider this assembly simply as one in which the irreversible entropy changes can be added to the reversible ones as small correcting terms. On the other hand, what are we to make of the undoubted fact that Kelvin's relations for the thermo-electric coefficients are in agreement with experiment, as are many analogous relations derived for other transport coefficients?

The answer to this difficulty is due to Onsager (1931), who discussed such assemblies, not from the point of view of pure thermodynamics, but from that of statistical mechanics or kinetic theory. (Palliative treatment having failed, something more radical must be resorted to.) He showed that Kelvin's relations, and others like them, must be deduced, not from a purely thermodynamical argument, but from the postulate of *microscopic reversibility*. By this we mean that, if an assembly or system is known at a certain time to be in state A, the probability that, at a slightly later time, it will be in state B is exactly the same as the probability that the same assembly or system, known initially to be in state B, will, after a similar time interval, reach state A. Put more succinctly, the postulate implies complete symmetry between past and future in the equations of motion of the microscopic systems. We postpone for a moment the examination of the evidence for this postulate. If we grant it, we can certainly derive relations of Kelvin's type. Without it, Kelvin's type of argument can only be saved by making some assumption additional to those of reversible thermodynamics. As an example of such an assumption we may mention the following: "If we increase the rate of supply of energy to an assembly in which dissipation of energy is already taking place, the rate of creation of entropy cannot diminish." If we assume this, and we instinctively recognise that it is correct, we can deduce Kelvin's relations fairly simply. Consider the circuit shown in fig. 6, consisting of two thermocouples maintained at different temperatures, T and $T+\Delta T$, with a potential difference E maintained by a battery. Then the rate of flow of heat is given by $\mathrm{d}Q/\mathrm{d}t=K\Delta T+\sigma I$ where K is a constant depending on the thermal conductivity and dimensions of the wires, while σ is the difference of the Thomson coefficients for the two metals. For the relation between E and I we have

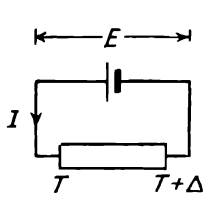

Fig. 6. Thermocouple circuit.

$$E=\Pi\Delta T+\rho I$$

where ρ depends on the resistivity and dimensions of the wires and Π is the Peltier coefficient. Then the rate of creation of entropy is

$$\left(\frac{1}{T}-\frac{1}{T+\Delta T}\right)\frac{dQ}{dt}+\frac{EI}{T}$$

(since heat is flowing from a temperature $T+\Delta T$ to a temperature T, and is being created at the rate EI)

$$=\frac{\Delta T}{T^2}(K\Delta T+\sigma I)+\frac{I}{T}(\Pi\Delta T+\rho I) \qquad (5)$$

By altering the applied potential E, we can vary I keeping ΔT constant, and the rate of creation of entropy is therefore a minimum if it involves only terms like I^2 and $(\Delta T)^2$, i.e. only if the terms involving $I\Delta T$ cancel, which leads just to one Kelvin's relation.

Onsager showed that results of this kind could also be deduced from the principle of microscopic reversibility or "detailed balancing", so that we have to examine the evidence for the soundness of this principle. First of all, it is a well-known principle of classical mechanics that, if we have an assembly of particles whose interactions are central (act along the lines joining each pair) then there is complete reversibility in time, i.e. if we have found a solution of the equations of motion, we can reverse all the velocities and get another solution. This result also holds if there are *magnetic* forces between the particles (provided that we exclude such cases as charged particles moving in the field of a permanent magnet the sign of whose field is kept constant after the reversal of all the particle velocities). In quantum mechanics, the equality of the probabilities of forward and reverse transitions follows if it may be assumed that all physically significant interactions can be represented by Hermitian matrices (as only then can we rely on the "result of a measurement" being a real number). This result is almost certainly correct, and represents the natural generalisation of the reversibility of the time-variable in classical mechanics. In this book, the postulate of microscopic reversibility will be assumed without further discussion, for which the reader is referred to treatises on quantum mechanics. The reader is referred to Onsager's two papers, and to de Groot's book *The Thermodynamics of Irreversible Processes* for a discussion of the consequences of this assumption from the thermodynamic point of view.

This assumption seems, however, to plunge us into worse difficulties than those that it seeks to remove. One at once asks how, if all the basic interaction processes between individual systems are reversible, such a thing as an irreversible process is possible at all. How, in fact, are we to account for such intrinsically "one-way" processes as heat conduction, diffusion and viscous damping? A proper understanding of

this question is important to us, because, as we have seen, such processes very often become more and more prominent as a transition point is approached, a fact which certainly calls for some explanation. The question of the microscopic description of macroscopically irreversible effects has been considered at great length by a number of workers, but it seems possible to sum up the basic facts fairly concisely.

3.6.2. Quantum-mechanical Description of Irreversible Effects

We shall formulate the problem for an assembly that can be described in quantum mechanics by a many-dimensional Schrödinger equation so that we are omitting relativistic and spin effects. The translation to the language of classical mechanics can readily be made if desired.

(a) Any assembly can be described by means of a set of wave functions, each consisting of a function ϕ_n of the co-ordinates of the individual atoms or molecules, multiplied by the time-factor $e^{-2\pi i E_n t/h}$ where E_n is the energy associated with the wave function ϕ_n. The assembly is then described by means of the combined wave function

$$\psi=\sum_n a_n\phi_n e^{-2\pi i E_n t/h}$$

If we have solved the Schrödinger equation completely, the a_n's will be constants. In practice we can seldom do this, but we may be able to find an approximate solution in which the a_n's are only varying slowly with time. (As an analogy, consider the case of two weakly coupled electrical circuits or pendulums. We can solve the problem *exactly* in terms of a pair of normal modes, corresponding to the two systems oscillating together in phase or in antiphase, or we can solve the problem *approximately* in terms of the oscillations of the two individual systems if we are prepared to admit that the amplitudes of these oscillations vary with time. The slower the variation, the weaker the coupling, hence the better this approximate solution.)

(b) The observable properties of the assembly will be described by expressions such as $\int \ldots \int \psi^* \mathbf{A} \psi d\tau \ldots$, where $\mathbf{A}$ is a linear operator corresponding to the property in question, and the integrations are to be carried out over the co-ordinates of all the particles. For example, the hydrodynamic particle-density ρ is determined as a function of x, y and z by integrating $\psi^*\psi$ over the co-ordinates of all the particles except one (particle 1 say) and then putting $x=x_1$, $y=y_1$, $z=z_1$. The corresponding operator is easily written down in terms of Dirac delta-functions. It is

$$\frac{1}{N}\sum_{n=1}^{N}\delta(x_n-x)\delta(y_n-y)\delta(z_n-z)$$

the summation over n preserving the symmetry between the N particles.

(c) The value of an "observable property", thus calculated, consists

of the sum of a number of terms constant in time together with others that oscillate at frequencies $(E_m-E_n)/h=\nu_{mn}$ where m and n are any two levels. There is, as yet, no trace of any "one-way" effects, all the observable properties of the assembly apparently *oscillating about mean values*. This seems to mean that, as time goes on, any observable quantity attains nearly the same value infinitely many times, and this seems to exclude all possibility of irreversible processes. (It does not seem to be possible to avoid this difficulty, as some have proposed, by pointing to the fact that an "observation" necessarily disturbs the assembly.)

(d) In general, however, the characteristic frequencies are *not* expressible as rational multiples of one another, in which case we may have to wait an exceedingly long time (the so-called Poincaré period of the assembly) before an observable quantity regains even approximately the value it had initially. In this respect the properties of "ideal" assemblies, such as the perfect gas in a cubical box, are definitely misleading. This special assembly has energy-levels that are all multiples of the quantity $h^2/8md^2$ where d is the side of the cubical box and m the mass of the gas-molecule. We might, therefore, expect such an assembly to repeat itself exactly at intervals of time $8md^2/h$ which is of the order of 10^4 seconds for light molecules such as helium or hydrogen in an enclosure of side ≈ 1 cm. In an actual gas, the characteristic frequencies are not exact multiples of $h/8md^2$ owing to the interactions between the atoms, and the Poincaré period of such an assembly is so much greater than 10^4 seconds that it becomes merely of academic interest. Suppose now that we have an assembly whose characteristic frequencies are distributed in a *continuous* spectrum, in contrast with the *discrete* spectrum characteristic of an ideal assembly such as the perfect gas. The behaviour of an observable quantity A will then be described by a function such as

$$A(t)=\int_{-\infty}^{+\infty} B(\omega)e^{i\omega t}d\omega$$

which is the limiting form taken, for example, by a Fourier series when the period (here the reciprocal of the H.C.F. of the characteristic frequencies) becomes exceedingly long. It is, of course, understood that the frequency function $B(\omega)$ obtained by substituting the wave function $\sum_n a_n\phi_n e^{-2\pi iE_nt/h}$ into the expression $\int \ldots \int \psi^* A\psi d\tau \ldots$ and then taking the Fourier transform of the result, may incorporate *discrete* parts, corresponding to well-marked characteristic frequencies of the assembly, e.g. absorption lines, and may also include regions of frequency in which the function $|B(\omega)|$ is zero or negligibly small. If, however, $B(\omega)$ is finite for ω zero and for a range of small values of ω then we may conclude that the quantity A will show "irreversible"

behaviour in the sense that one must wait an extremely long time before A returns to its old value. For consider the Fourier transform of a function such as

$$f(t)=0 \quad (t<0)$$
$$f(t)=e^{-\lambda t} \quad (t>0)$$

which is typical of functions that take a maximum value at the origin and then decrease irreversibly. The corresponding frequency function $g(\omega)$ is $1/(\lambda-i\omega)$, whose modulus is $1/(\lambda^2+\omega^2)^{1/2}$, which has a maximum value at $\omega=0$ and decreases slowly as ω increases. We may conclude that a frequency function $B(\omega)$ that is finite for $\omega=0$ is associated with irreversibility. *"Irreversible" processes are thus the result of transitions between levels whose energy is nearly the same, so that the Bohr frequency is small.*

In the standard theory of the absorption and scattering of light according to perturbation theory, we assume that energy is conserved "in the mean". Processes violating conservation merely lead to rapid *oscillations* in quantities like a_n, but not to "one-way" or irreversible processes. To get a transition probability that *increases with time steadily* conservation of energy is necessary. See any text-book on quantum mechanics. Given the function $B(\omega)$ one could, in principle, calculate the behaviour of A as a function of time. In practice, such information is not usually available for an actual assembly and we have to proceed from the very fragmentary information that is available, e.g. from quantum-mechanical perturbation theory. There are very few cases where the calculation can actually be carried through to the point of predicting the magnitude of the decay constant. As a typical example of such a calculation, we may mention the calculation of the viscosity of a gas. Here we can identify the only process that can contribute effectively to the viscosity, namely a two-body collision in which energy is conserved. (A three-body collison is rare at ordinary gaseous densities, while a two-body collision that implied a finite value of the energy-difference E_m-E_n between the initial and final configurations would contribute only *rapidly oscillating* terms to $A(t)$.) If we begin with the gas being uniformly sheared, we can calculate the rate at which the momentum is redistributed by two-body collisions occurring at various angles of impact, and this is really equivalent to a calculation of $B(\omega)$ at $\omega=0$ and for a small range of values of ω on either side of zero. This is then enough to enable us to calculate the rate of decay of the shear, hence the viscosity.

In order to get a function $B(\omega)$ that is finite for a range of values of ω about zero, it is evident that our assembly must possess a continuous or nearly continuous *range* of energy-levels (not necessarily centred about an energy of zero). We shall not attempt the difficult task of

actually calculating one of the time-constants associated with a transport process in a co-operative assembly, indeed it is doubtful whether such a calculation has ever been carried out *ab initio*. We have outlined the basic theory of irreversible processes because it seems to provide a slight clue to the reason why they often become especially important in the neighbourhood of a transition point. We have seen that the "crowding together" of energy-levels favours an irreversible process. Now Onsager (1944), in his discussion of the nearest neighbour model, showed that, at the Curie point, there was a very large number (infinitely many in an infinite assembly) of possible complexions, all with practically the same Boltzmann factor, and therefore practically the same energy. At temperatures other than the Curie point the most probable complexion is separated by a finite energy gap from the remaining possible complexions, though some of the latter still form a continuum. Now the type of Curie point found by Onsager (1944) is almost certainly of the type C discussed in Chapter II, and arises from the second derivative of the partition function with respect to temperature becoming "infinite", as is almost certainly true also of the second derivative with respect to magnetic field. By a suitable transcription of the argument given in Chapter II, we should conclude from this that $\partial E/\partial S$, $\partial^2 E/\partial S^2$, $\partial E/\partial I$, $\partial^2 E/\partial I^2$ all vanish at the Curie point, which can only mean that we have a large number of complexions all of nearly the same energy as the most probable one. This is just the condition that leads to irreversible effects becoming prominent. This argument perhaps puts on a sounder basis the intuitive approach given on p. 33 in which we compared the situation as we approach the Curie point with that of a mechanical system which was apparently approaching instability due to the progressive weakening of the controlling force. We pointed out also that, while we can set up a reasonable analogy between the behaviour of E as a function of S, I or ρ in a statistical assembly and the behaviour of the potential energy V as a function of a displacement x in a mechanical system, there was no obvious analogy of the "effective mass" that occurs in the latter case. (A quantum-mechanical calculation would proceed by taking an appropriate average over the transition probabilities between levels, which takes us outside the province of statistical mechanics.)

3.7. The Description of Metastable States in Statistical Mechanics

As we have already stated, we may approach the theory of a change of state from the point of view of statistical mechanics in two distinct ways. We may attempt a detailed theory starting from a known or assumed intermolecular interaction, or we may, as in the older theories, attempt semi-empirical corrections of an ideal model such as the

"perfect gas" or "Langevin assembly" (of non-interacting atomic magnets). This latter approach leads to implicit equations, and there is, in general, no difficulty in interpreting the existence of two or more solutions of such an equation, which correspond to the possible existence of two or more separate phases. This approach enables us to give a satisfactory account of such phenomena as the existence of metastable states, superheating, supercooling, etc. When we attempt the former, more fundamental approach, the position is (apparently) not so satisfactory. When we consider the Mayer theory of liquids, we conclude that, below the critical point, the isotherms resemble those shown in fig. 4, except that they consist, for example, of the portions of the curve DE and IJ, together with the straight line EGI, with *no trace of* the metastable portions EF and HI. These portions, which are given by a simple theory of van der Waals type, undoubtedly correspond to physical reality. Why, then, are they absent in what purports to be a *more rigorous* statistical treatment of evaporation and condensation?

The answer to this question lies, not in any error or inadequacy in Mayer's treatment, but in a deep-seated limitation of statistical mechanics. A statistical-mechanical treatment usually begins with a "closed" assembly in which the energy and number of particles are both held constant, and from this the properties of an "open" assembly, which is permitted to exchange energy with the outside world, the temperature being specified instead of the energy, can then be deduced thermodynamically. Now if we take the "closed" assembly, the calculation of a quantity such as the pressure proceeds by the following steps:

(a) We suppose that we know, or can guess, the possible energy-levels of the assembly, a multiple level being counted repeatedly.

(b) We construct the function $f(z)=\sum_r z^{\epsilon_r}$ where the summation is over all physically distinguishable energy-levels, ϵ_r, of the whole assembly. In practice the energy-levels of the whole assembly are usually not considered explicitly, but are inferred indirectly by breaking down the assembly into approximate normal modes (e.g. sound waves or single particle energy-levels) and then considering the number of ways in which these modes can be occupied.

(c) For a "closed" assembly we select from $f(z)$ the coefficient of z^E, where E is the specified total energy of the assembly. This coefficient is the number of physically distinguishable ways in which the assembly can assume this energy. Let this coefficient be $W(E)$.

(d) We now make the assumptions that the assembly is equally likely, at any given instant of time, to be in any one of these $W(E)$ complexions, and that it will, in the course of time, work through all of them, spending an equal time in each, in other words, that all complexions of the correct energy are equally probable.

(e) On these assumptions we can calculate the average value of any quantity X. For let X_r be the value of X if the assembly is known for certain to be in the rth complexion of energy E_r. Now E_r will either be of the correct energy E, in which case the complexion will have a finite probability of occupation, or else it will be of the wrong energy and will never be occupied at all. The average value of X will then be

$$\overline{X}=\frac{\text{coeff. of } z^E \text{ in } \sum_r X_r z^{\epsilon_r}}{\text{coeff. of } z^E \text{ in } \sum_r z^{\epsilon_r}} \tag{6}$$

As, an example, the calculation of the pressure is equivalent to a calculation of the average value of $-(\partial\epsilon_r/\partial V)$ (the average work done if the volume of the assembly is changed slightly).

(f) The process of selection of the coefficient of z^E can usually be done sufficiently accurately for a large assembly, by contour integration by the method of steepest descents, and the value of X is then given sufficiently accurately by $\overline{X}=\sum_r X_r\theta^{\epsilon_r}/\sum_r \theta^{\epsilon_r}$, where θ is the real value of z which makes $z^{-E}\sum_r z^{\epsilon_r}$ a minimum, that is $E=\theta(\partial/\partial\theta)(\log f(\theta))$.

(g) Comparison of this formula for the average or "equilibrium" value of X with those of thermodynamics leads us to make the following identifications between the variables of thermodynamics and statistical mechanics:

$$\theta=e^{-1/kT}, \qquad F=-kT\log f(\theta)$$

and this enables us to infer the properties of an "open" assembly, in which we specify the temperature, from those of the "closed" one in which we specify the energy.

For a fuller account of these various steps and the arguments used to justify them, the reader is referred to treatises on statistical mechanics. We have summarised the various steps in order to show which of them are open to doubt.

(a) calls for no comment.

(b) offers no difficulties in principle. In practice, the simplest way to deal, for example, with a "perfect gas" type of model may be to consider the occupations of the "one-particle" levels, and then to use a second selector variable and contour integration in order to make sure that the total of the occupation numbers is equal to the total of the elementary particles present. This may lead to difficulties of technique but not of principle.

(c) is rigorously correct.

(d) is discussed below.

(e) is a logical consequence of (d). If each accessible complexion is equally probable, averages must be calculated in this way, the rth

complexion being weighted according to the corresponding value of the desired quantity X.

(f) The method of steepest descents applied to the evaluation of the contour integrals usually gives a sufficiently accurate result, but cases, admittedly rather artificial, can be constructed in which the method fails to give the right result. See Haselgrove and Temperley (1954). In other words, the "mean" state is not *always* the same as the "most probable" state of an assembly, even when the assembly is large, but this is only of academic interest at present.

(g) is a logical consequence of (f).

Thus, it is only assumptions (d) that are open to serious doubt. These have received very careful consideration from the mathematical point of view. The so-called "ergodic hypothesis" (that an assembly will, in the course of time, work through all *accessible* complexions, i.e. all those with the correct energy) is almost certainly a sufficiently close approximation for a real assembly (though it is false for the perfect gas because all the frequencies are integral multiples of $\boldsymbol{h}/8md^2$). If the ergodic hypothesis, or some slightly weaker statement, be granted it is easy to make plausible the further postulate that all accessible complexions are to be taken as equally probable, though this has not yet been proved for a *single* assembly, but only for a large group of identical assemblies (the so-called "ensemble") considered as a whole.

If we accept the above arguments, then it becomes quite clear that the statistical average value of any observable quantity can have one value only, the value obtained by averaging over *all* the accessible complexions. This precludes curves such as those shown in fig. 4, in which multiple values are possible, but does *not* preclude, for example, an isothermal such as DEGIJ with *sharp corners* at E and I (the corners being mathematically sharp only in the limiting case of a very large assembly), but this would mean that a metastable equilibrium was not possible.

The flaw in the argument seems to be that we do *not*, in practice, average over a time comparable with the Poincaré period of an assembly in the course of making observations on it. If, however, we average over a shorter period, then the complexions assumed in succession by the assembly bear some definite relation to the one the assembly was in at $t=0$. We then have to consider whether or not the assembly assumes, during a time "comparable with that of doing an experiment", a *representative selection* of all the possible complexions energetically open to it. If it does, then our process of averaging over *all* accessible complexions will give the correct answer, and we may then infer the absence of metastable states, otherwise we cannot do this.

We may illustrate the various possible types of behaviour by considering a very simple assembly with two degrees of freedom only, namely a mass mounted on two springs at right angles to one another (not necessarily of the same strength) (fig. 7). Then, if we suppose that it is supplied initially with a certain amount of energy, the mass is energetically capable of reaching any point within a certain rectangle, and various kinds of trajectory are possible.

(a) If the two periods are equal, or in a simple rational ratio, the trajectory is an ellipse or a simple Lissajous figure, which continually repeats itself.

(b) If the ratio of the two periods is irrational, the Poincaré period of the assembly becomes infinite. The trajectory then, in time, "fills up" the whole rectangle uniformly. (More precisely, by waiting a sufficiently long time, we can expect to see it approach as closely as we please to any specified point.)

(c) If the ratio is irrational, but very nearly an integer, the trajectory is very nearly a simple Lissajous figure, and only departs very slowly from its initial form, so that the part of the rectangle in which the mass is likely to be found depends very much on the initial conditions.

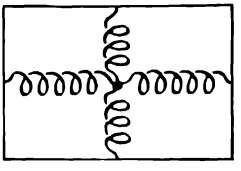

Fig. 7.
Simple mechanical systems.

Case (a) is unlikely ever to be realised exactly in practice, though the perfect gas in a cubical box (p. 39) *is* of this general type. Case (c) indicates that we may easily get an assembly for which the ergodic hypothesis is correct, which, nevertheless, has accessible complexions that can be divided into two or more groups. It is then quite possible that the assembly goes from one group of complexions to another only in a time comparable with the Poincaré period, i.e. the time taken for the assembly to work through *all* the complexions. If this is so, it is possible to understand the existence of metastable states. We can then recognise that the average properties of an assembly, taken over any reasonable time, *may* depend on the initial complexion, whereas, in an absolutely strict application of statistical mechanics, only *one* value of any average property is permissible.

We have already seen that we must pay attention to the existence of the Poincaré period of an assembly in order to account properly for irreversible effects. The existence of these, and of metastable states, is so bound up with changes of state that a theory that does not provide a framework for dealing with them is of little value. We therefore agree that, according to the nature of the assembly, averaging is to be carried out, *either*

(a) Over all accessible complexions, *or*

(b) Over those complexions in the same "group" as the initial one (it being understood that there may be no definite boundary between the "groups").

It sometimes happens that a relaxation time is *comparable* with the "time of doing an experiment". The classic example of this is a dielectric with permanent dipoles, and we get irreversible effects if the period of oscillation of an applied field is comparable with the time taken by the dipoles to orient themselves, but not if it is much shorter or much longer. In the two limiting cases, we may still use a statistical mechanical treatment, but the intermediate case usually has to be handled by kinetic theory.

3.8. Relationship with Fluctuation Theory

Besides enabling one to predict the equilibrium configuration of an assembly whose accessible energy-levels may be supposed approximately known, statistical mechanics can also give us certain rather general indications of the extent to which the assembly is likely to *depart* from the predicted equilibrium—that is, quantitative estimates of the "fluctuations" are possible. We leave aside the difficult question of how far it is permissible to use equilibrium theory to compute spontaneous *departures* from equilibrium. The easy answer would seem to be that, if our computed fluctuations about equilibrium are relatively small, then our assembly does indeed spend nearly all of its time in configurations closely resembling the equilibrium one. There are, however, cases in which the calculated fluctuations become *large*, and yet for which we still believe equilibrium theory to be valid. As one might expect, this sort of situation is often associated with an approaching transition—the fluctuations about the mean configuration become bigger and bigger and finally result in complete instability.

It is remarkable that equilibrium theory is able to give us any information at all on such matters, because, as we have seen, it contains no explicit reference to time-intervals or transition probabilities. The method that we shall use has in some cases, such as that of Brownian movement, been checked by comparison with kinetic theory, but, since the number of types of assembly which can be treated by kinetic theory with any real degree of rigour is quite small, and since such types of assembly almost invariably show *small* fluctuations, the application that we are about to make is an extrapolation. However, comparison with the purely thermodynamic study of assemblies near a transition point raises several points of interest.

We recall the standard formula for the occupation of a level of energy ϵ_r and multiplicity g_r:

$$\bar{n}_r = \frac{g_r}{\lambda^{-1} e^{\epsilon_r/kT} \pm 1} \tag{7}$$

If we refer to the derivation of this result, we find that it results from the following averaging process (the generalisation to a multiple level is made readily):

$$\bar{n}_r = {}_{Av}\left[\sum_s \left\{ s(xz^{\epsilon_r})^s \binom{g_r+s-1}{s} \right\} \Big/ \sum_s \left\{ (xz^{\epsilon_r})^s \binom{g_r+s-1}{s} \right\}\right] \text{(Bose-Einstein)} \tag{8}$$

$$\bar{n}_r = {}_{Av}\left[\sum_s \left\{ s(xz^{\epsilon_r})^s \binom{g_r}{s} \right\} \Big/ \sum_s \left\{ (xz^{\epsilon_r})^s \binom{g_r}{s} \right\}\right] \quad \text{(Fermi-Dirac)} \tag{9}$$

the two different types of expression catering for the two different types of statistics.

The calculation of these "average occupation numbers", which are really weighted sums of the probabilities that the level is occupied 0, 1, 2, . . . times, can be carried out sufficiently accurately if we replace x and z by their critical values λ, $e^{-1/kT}$ corresponding to the most probable state. Expressed in mathematical terms, this is equivalent to saying that additional factors such as the extra factor s in the numerators of expressions (8) and (9) can be introduced into the Fowler-Darwin contour integral without appreciably shifting the positions of the saddle-points, so that their effect is practically that of multiplying the integral by a factor. For a full discussion of the validity of such assumptions, the reader is referred, for example, to Schrödinger's *Statistical Thermodynamics* or Fowler's *Statistical Mechanics*. In our calculations of fluctuations other weighted sums, associated with each level, appear, and we shall make the assumption that they can also be calculated according to equilibrium theory, even when their values imply considerable temporary departures from the equilibrium state. This assumption is discussed in detail by Fowler, who shows that the results derived on the basis of such assumptions are formally correct. A deeper argument than the conventional one we have just outlined is needed in some cases. For example, a quantity that is often used as a rough measure of the departures from equilibrium is the mean-square deviation of a particular occupation number, that is, the quantity $(n_r-\bar{n}_r)^2$ averaged over all physically permissible configurations of the assembly. The difficulty about averaging such functions as this is that the corresponding leading terms in the Fowler-Darwin contour integral may cancel, and we may need an argument of more delicate type than one which is suitable for establishing the value of $\bar{n}_r$ itself. We do not wish to enter into this argument, because the assumption that $(n_r-\bar{n}_r)^p$ can be averaged by using just the same rules as those for n_r is, in fact, correct. What we do wish to emphasise is that the application of fluctuation theory near a transition point involves a chain of no less than three distinct assumptions, which we recapitulate here.

(a) That it is permissible to use a method of averaging devised for equilibrium conditions for assessing *departures* from equilibrium. This is bound up with the question referred to above (p. 35), namely, in what conditions is it reasonable to define a quantity such as the entropy under non-equilibrium conditions?

(b) That, assuming the validity of (a), it is permissible to use the same formal *methods* for averaging equilibrium quantities and fluctuations.

(c) That (a) and (b) remain valid near a transition, when, as we shall see, fluctuations can and do become large.

Of these, only the validity of (b) seems to have been made reasonably certain by Fowler's improved treatment. (a) almost certainly has *some* range of validity, but that of (c) remains an open question. We shall use it until something better is discovered. To obtain the average value of $(n_r-\bar{n}_r)^2$, we write this average as $\overline{n_r^2}-2\bar{n}_r.\bar{n}_r+(\bar{n}_r)^2$ or as $\overline{n_r^2}-(\bar{n}_r)^2$, and $\overline{n_r^2}$ is to be calculated by replacing the extra factors in the numerators of expressions (8) and (9) by s^2. The formulae required can be written more compactly as follows:

$$\bar{n}_r=\lambda\frac{\partial}{\partial\lambda}\log\{(1\mp\lambda e^{-\epsilon_r/kT})^{\mp g_r}\}\quad\begin{cases}-\text{B.-E.}\\+\text{F.-D.}\end{cases}\tag{10}$$

$$\overline{n_r^2}=\left(\lambda\frac{\partial}{\partial\lambda}\right)^2\log\{(1\mp\lambda e^{-\epsilon_r/kT})^{\mp g_r}\}\quad\begin{cases}-\text{B.-E.}\\+\text{F.-D.}\end{cases}\tag{11}$$

the operation $\lambda\partial/\partial\lambda$, where λ is the "saddle-point" value of x, corresponds to the insertions of the extra s-factors in the numerators of (8) and (9). We are assuming, then, that each of the terms in (8) and (9) represents the probability of finding the rth group of levels occupied exactly s times. Performing the operations indicated by (11) we find

$$\overline{(n_r-\bar{n}_r)^2}=\overline{n_r^2}-(\bar{n}_r)^2=\bar{n}_r\pm\frac{(\bar{n}_r)^2}{g_r}\quad\begin{cases}+\text{B.-E.}\\-\text{F.-D.}\end{cases}\tag{12}$$

These results do *not* reduce to the classical result $\bar{n}_r+(\bar{n}_r)^2/N$, the difference being due to "classical" atoms being "labelled" while in quantum statistics they are not. Another result can be obtained for the average fluctuations of the energy. Starting from the standard result

$$\bar{E}=\sum_r\bar{E}_r=\sum_r\frac{\epsilon_r\lambda e^{-\epsilon_r/kT}}{1\mp\lambda e^{-\epsilon_r/kT}}$$

we can deduce, by the same averaging process, the following results:

$$\overline{E^2}=\sum_r\overline{E}_r^2+\sum_{r\neq t}\overline{E_rE_t}$$
$$=\sum_r\frac{\epsilon_r^2\lambda e^{-\epsilon_r/kT}}{1+\lambda e^{-\epsilon_r/kT}}+\sum_{r\neq t}\frac{\epsilon_r\lambda e^{-\epsilon_r/kT}.\epsilon_t\lambda e^{-\epsilon_t/kT}}{(1+\lambda e^{-\epsilon_r/kT})(1+\lambda e^{-\epsilon_t/kT})}\quad\text{(F.-D.)}$$

$$(\bar{E})^2=\sum_r \frac{\epsilon_r{}^2\lambda^2 e^{-2\epsilon_r/kT}}{(1+\lambda e^{-\epsilon_r/kT})^2}+\sum_{r\neq t}\frac{\epsilon_r\lambda e^{-\epsilon_r/kT}.\epsilon_t\lambda e^{-\epsilon_t/kT}}{(1+\lambda e^{-\epsilon_r/kT})(1+\lambda e^{-\epsilon_t/kT})} \quad \text{(F.-D.)}$$

so that we have

$$(E-\bar{E})^2=\overline{E^2}-(\bar{E})^2=\frac{\lambda\epsilon_r{}^2 e^{-\epsilon_r/kT}}{(1+\lambda e^{-\epsilon_r/kT})^2}=kT^2\frac{\partial\bar{E}}{\partial T} \quad \text{(F.-D.)} \qquad (13)$$

For the Bose-Einstein case we have a slightly different generating function to help us calculate $\overline{E_r{}^2}$, because E_r may assume the values of $0, \epsilon_r, 2\epsilon_r, \ldots$ while in the Fermi-Dirac case, the only possibilities are $0, \epsilon_r$. The generating function for E_r is, in the B.-E. case:

$$\epsilon_r\lambda e^{-\epsilon_r/kT}+2\epsilon_r\lambda^2 e^{-2\epsilon_r/kT}+3\epsilon_r\lambda^3 e^{-3\epsilon_r/kT}+\ldots$$

leading to

$$\bar{E_r}=\frac{\lambda\epsilon_r e^{-\epsilon_r/kT}}{1-\lambda e^{-\epsilon_r/kT}}$$

as usual, while that for $\overline{E_r{}^2}$ is

$$\epsilon_r{}^2(\lambda e^{-\epsilon_r/kT}+4\lambda^2 e^{-2\epsilon_r/kT}+9\lambda^3 e^{-3\epsilon_r/kT}+\ldots)$$

which leads to

$$\overline{E_r{}^2}=\frac{\epsilon_r{}^2(\lambda e^{-\epsilon_r/kT}+\lambda^2 e^{-2\epsilon_r/kT})}{(1-\lambda e^{-\epsilon_r/kT})^2}$$

so that we have again

$$(E-\bar{E})^2=kT^2\frac{\partial\bar{E}}{\partial T} \quad \text{(B.-E.)} \qquad (14)$$

the cross terms cancelling out in the same way as before. Either of these derivations applies to the classical case in the limit, and it makes no difference in either case whether we consider energy-levels separately, or if some of them are degenerate and we group them together.

By an obvious extension of this work, we can deduce relations between the averages of higher powers of $(E-\bar{E})$ and higher temperature derivatives of the specific heat. Since nearly every phase transition probably involves an "infinity" in the specific heat, or in *some* derivative of it, we may expect an approaching transition to manifest itself by a fluctuation of *some* power of $(E-\bar{E})$ increasing without limit. Thus if Ehrenfest (1933) had formulated his idea of "orders of phase-transitions" in a slightly different way, by reference to these fluctuations, he could probably have covered all types of case, though the classification might be rather less precise than that already introduced in Chapter II. (There would remain the hypothetical case, Tisza (1949), of a change of state occurring without any significant change of entropy, in which case some other thermodynamic variable would show large fluctuations from the mean.) Neglecting such changes, we might classify as follows:

Discontinuity in $\bar{E}$ (latent heat)	First-order transitions. (Type A, Chapter II.)
$(E-\bar{E})^2$ shows large fluctuations. $C_v \to \infty$	Tisza type transitions. (Type C, Chapter II.)
$(E-\bar{E})^3$ shows large fluctuations. $\partial C_v/\partial T \to \infty$	Ehrenfest's second-order transitions. (Types B_1 and B_2, Chapter II.)
$(E-\bar{E})^4$ shows large fluctuations. $\partial^2 C_v/\partial T^2 \to \infty$	e.g. the transition of a perfect Bose-Einstein gas (p. 303).

As examples of assemblies where we do seem to have fluctuations on a macroscopic scale, due to the "thermodynamic driving force" approaching zero, we may mention the following:

(a) A liquid near its critical temperature. The phenomenon of opalescence due to large fluctuations of density has often been discussed, and there is evidence (p. 87) that such an assembly is sensitive to impurities or small changes in the external conditions.

(b) The liquid He II film (p. 299). Again it appears, theoretically and experimentally, that the top layers of this film are extremely weakly bound, and are sensitive to small perturbations such as gravity and to the incidence of weak radiation. Bowers (1953).

(c) The intermediate state of a superconductor. Here it seems, both theoretically and experimentally, that there are a multitude of possible domain structures differing very slightly in free energy, so that the one that is actually realised depends very much on the previous history of the specimen. Kuper (1951).

A type of assembly that cannot be realised experimentally (the perfect Bose-Einstein gas) shows extremely strange fluctuation behaviour—the possible fluctuation of $(n_0-\overline{n_0})^2$ being comparable with $\overline{n_0^2}$ instead of with n_0 as for an ordinary assembly. This behaviour is confined to n_0 (the suffix zero referring to the level of lowest energy) as the other n_r's are all small compared with unity, even below the transition temperature. Thus, it would seem that states will often be realised in which n_0 differs widely from its mean value $\overline{n_0}$, whereas in an ordinary assembly the probability of this is small. Since the lowest level has no energy or entropy, the only "thermodynamic driving force" tending to "resist" changes in n_0 is an *indirect* one, arising from the fact that a change of n_0 in a closed assembly results in consequential changes in the other n_r's, since the sum of all the occupation numbers is constant. To a first approximation such changes would leave the free energy constant. Another point that seems to call for comment is that some writers have claimed that certain physical quantities may become non-analytic in the neighbourhood of a transition—for example, Zimm's

suggestion (1951) that all the volume derivatives of P along the critical isotherm (not merely the first two) may vanish at the critical point. Such a situation would formally invalidate certain formulae, for example, Smoluchowski's treatment of fluctuations near the critical point as presented by Fowler (1936), but this would apparently not introduce any difficulty of principle. It seems that such a situation would mean no more than that calculations would have to be made numerically from actual experimental data on the equation of state instead of analytically from some assumed equation of state.

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CHAPTER IV

Evaporation and Liquefaction

4.1. Possible Liquid Models

It may seem surprising that we are able to give physically satisfying accounts of evaporation and liquefaction when we have no completely satisfactory model of the liquid state itself. We shall consider five types of theory:

(a) The "imperfect-gas" type of theory, in which molecular interactions are allowed for on a semi-empirical basis.

(b) The "cell" or "free-volume" type of theory, in which we attempt to relate the properties of a liquid to those of a typical molecule in a "smoothed field" representing the effect of interactions with the remaining liquid.

(c) The "hole" type of theory, in which we think of a liquid as a "debased" crystal lattice which has lost its long-range order.

(d) Attempts to compute directly the "distribution function" of the liquid, given the interaction function, and to locate the temperatures at which the analytic form of the distribution function changes.

(e) The Mayer-type theory, which tries to show that liquefaction is a rigorous consequence of the existence of intermolecular interactions of a certain type.

All of these, except the imperfect-gas type of theory, are, in principle, capable of being developed so as to include evaporation and solidification within the framework of a single theory, but (d) and (e) look the most promising lines of approach at present, types of theory such as (b) and (c) always seeming to require a number of *ad hoc* assumptions.

Various writers have claimed that the existence of attractive-repulsive forces of Lennard-Jones type between molecules ($V=-Ar^{-m}+Br^{-n}$, $n>m$) implies a periodic lattice structure at sufficiently high densities and low temperatures. So far, this is the only type of interaction on which theories of fusion or evaporation have been based, and we do not consider, for example, metallic binding, which is a collective effect and cannot be properly represented as a sum of interactions between *pairs* of atoms or molecules. The *precise* conditions for the formation of a solid-like periodic lattice, in preference to a liquid-like amorphous structure, have not yet been formulated, even for a Lennard-Jones type of interaction. However, we always have basically the same

situation in a solid, a lattice structure is produced by some sort of balance between attractive and repulsive forces, even though these forces cannot be represented in any simple way. In liquid, it is better to think of a rough balance between the net effect of intermolecular forces and the effect of thermal agitation. The density of a liquid is usually a few per cent less than that of its solid, in which case the intermolecular distances are slightly greater, and we may expect the effect of intermolecular forces to be, on the whole, attractive. The situation is illustrated very well by certain liquid models, e.g., Born and Green (1947) in which the actual external pressure appears in the theory as the difference between two large terms. One of these is comparable in magnitude with the "gas kinetic pressure" NkT, representing the effect of thermal agitation, while the other represents the opposing effect of intermolecular forces. (See also equation (1) below, in which the pressure of a van der Waals gas is represented in a similar way.)

A liquid seldom has any definite "repeating" lattice structure, the configuration in the neighbourhood of a typical molecule being described instead by means of the "distribution function" (fig. 8). This function, $g(r)$, is proportional to the number of molecules likely to be found in any small volume at a distance r from the centre of a certain specified molecule. From X-ray studies, it has been deduced that the variation of $g(r)$ with distance is of the type shown in fig. 8. Such a structure is just of the type to be expected on the basis that one has approximately spherical molecules randomly packed. (A neat *experimental* proof of this statement was given by Hildebrand and Morrell (1936).) If we treat the cores as rigid spheres of radius r_0, no two molecules can approach closer than a distance $2r_0$, so that $g(r)$ is effectively zero for $r<2r_0$. Now it is theoretically possible to pack as many as twelve spheres round a central one, so that a rapid rise in $g(r)$ is to be expected when r passes through the value $2r_0$. If, on the average each molecule is surrounded by, say, nine others, as seems to be a reasonable figure for a liquid, de Boer (1952), the presence of these nine will prevent any more molecules from approaching the central molecule much closer than $4r_0$, so that we are led to the picture of our typical liquid molecule being surrounded by "Chinese boxes", that is we expect $g(r)$ to fluctuate with distance from a typical molecule in just the sort of way shown in fig. 8. For a discussion of distribution functions and the methods of deducing them from X-ray data, the reader is

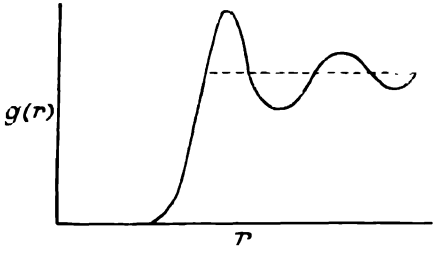

Fig. 8. Distribution function of a liquid.

referred to Frenkel, *Kinetic Theory of Liquids*, Chap. 3, while the influence of the interatomic force on the distribution function has been studied by Kirkwood and his collaborators in a series of papers (1935 onwards). Their work makes it likely that a distribution function of the type shown in fig. 8 is the correct consequence of almost any reasonable law of intermolecular force of the usual "attractive-repulsive" type. For the remainder of this chapter, we shall be using classical statistics, according to which the kinetic and potential energies can be dealt with independently in a statistical mechanical treatment. For the partition function may be written

$$f=\int_{\dots 6N\dots}\exp\{(-\mathrm{T}-V)/\boldsymbol{k}T\}\mathrm{d}x_i\mathrm{d}y_i\mathrm{d}z_i\mathrm{d}p_x^{(i)}\dots i=1\to N$$

general theory (see, for example, Rushbrooke, *Statistical Mechanics*) calling for equal weighting of all possible complexions, that is for integrations over all permissible co-ordinates and momenta of all the molecules, after inserting the appropriate Boltzmann factor for each complexion of the assembly. Now, we may suppose that the potential energy V is independent of the momenta and depends only on the positions of the molecules (which should be correct to a high approximation), while the kinetic energy T depends only on the momenta (which is certainly correct). If the exponential factor can be written $\exp(-\mathrm{T}/\boldsymbol{k}T).\exp(-V/\boldsymbol{k}T)$, the integrations over the co-ordinates and momenta can be carried out separately. T may be written

$$\frac{1}{2m}\sum_i(p_x^{(i)2}+p_y^{(i)2}+p_z^{(i)2})$$

The factor in f depending on $p_x^{(i)}$ is $\exp(-p_x^{(i)2}/2m\boldsymbol{k}T)$, which, integrated over all possible values of $p_x^{(i)}$ between $\pm\infty$, leads to a factor $(2\pi m\boldsymbol{k}T)^{1/2}$ for each of the $3N$ momenta. The average kinetic energy is always $(3/2)N\boldsymbol{k}T$ for such an assembly, irrespective of the variation of V with the co-ordinates. However, it is only in a classical assembly that this last step is legitimate. In a quantum assembly T and V have to be treated as operators which do not commute, in which case the product rule for exponentials does not hold. The integral must then be replaced by the Slater sum-over-states.

If the assembly may be treated as classical in the sense just explained, it is possible to calculate the internal energy from the observed distribution function. The pressure and entropy can, in principle, be computed if we know also the variation of $g(r)$ with density and temperature, and a comparison with observed values would then enable us to check the accuracy of our assumption that the interactions are of Lennard-Jones type. In practice, the experimental knowledge of $g(r)$ is incomplete in various ways, especially for r small, because X-ray scattering at high angles is hard to observe, so that the comparison just suggested has never, in fact, been carried out.

4.2. Attempts at Theoretical Calculations of the Distribution Function

In principle, it ought to be possible to develop a complete theory of liquids, including fusion and evaporation, on the following lines:

(a) From an assumed interaction function $V(r)$ calculate the corresponding $g(r)$ as a function of density and temperature.

(b) From this $g(r)$ calculate the interaction energy and hence the equilibrium properties of the liquid.

If we know the distribution function as a function of r, it is possible to calculate the average potential energy as long as one may assume that the forces between molecules are central and act between pairs of molecules only, i.e. if the interactions are of Lennard-Jones type, and if the interaction energy between two molecules is unaffected by the proximity of a third. For, under these conditions, we have for the potential energy between an average pair of molecules,

$$\overline{V}_{1,2}=\int_0^\infty V(r)r^2g(r)\mathrm{d}r \Big/ \int_0^\infty r^2g(r)\mathrm{d}r$$

the total number of interacting pairs in an assembly of N molecules being $N(N-1)/2$.

If, further, we regard the assembly as being "classical", we also know the kinetic energy and therefore the total energy as a function of density and temperature, and then the entropy, pressure and other thermodynamic quantities can be derived by means of the usual formulae of thermodynamics.

(c) Compare the values of the Gibbs function per mole (partial potential) with those obtained:

(1) For a periodic lattic (solid);
(2) For a random arrangement (gas).

the equilibrium curve separating two phases being obtained by equating partial potentials. See Chapter II.

In practice, this complete programme has never been carried out, though various parts of it have been attempted. For example, Born and Green (1947) and Kirkwood *et al.* (1935 onwards) have arrived at approximate integral equations satisfied by $g(r)$, but further approximations are needed in order to solve these equations, and the results are not sufficiently accurate to enable parts (b) and (c) of the above programme to be carried through. One reason for this can be seen if we go back to van der Waals's equation. We may write it as

$$P=\frac{NkT}{V-b}-\frac{a}{V^2} \qquad (1)$$

Now we know that, except near the critical point, the specific volume of a vapour is always very much greater than that of its liquid. For the vapour, V is large compared with b and a/V^2 is small. For the liquid, V will be comparable with b and a/V^2 will be large. In other words, the two physically relevant values of V correspond respectively to the vapour, which behaves like a nearly perfect gas, and to the liquid, for which the external pressure is the difference of two large terms, one the result of thermal agitation, the other depending on the net attractive forces. Any inaccuracy in the calculation of either term is likely to have a disproportionately large effect on the predicted pressure. This is the same situation that we have already noticed in connection with the theory based on the use of the distribution function. (Born and Green (1947).)

These difficulties are not, however, insuperable, and it is already possible to see how a combined treatment of fusion and evaporation is likely to develop. Since the "damped" distribution function seems to be one of the characteristic features of the liquid state, in contrast both with the periodic structure of the solid and with the random structure of a nearly perfect gas, it seems certain that any ultimately successful theory, covering both changes of state, will have to take explicit account of the distribution function. It is therefore attractive to sketch the programme for such a theory. As a matter of fact, two distinct types of approach are possible. We may attempt a direct computation of the distribution function, the interaction energy being supposed given, and we then look for characteristic changes in its mathematical form as we approach the solid or vapour regions in the diagram of state, or we may include a study of the distribution function as a natural development of the Mayer theory to be described below (p. 77). For the present, we are concerned with the former type of approach.

At present, there is no known method of computing the theoretical distribution function from an assumed interaction function unless a number of approximations are made. Unfortunately, these are such that their numerical effect is extremely hard to assess. For example, we do not even yet know the exact equation of state for the physically very simple assembly of non-attracting rigid spheres, much less the correponding distribution function. Such information, when it becomes available, would enable *numerical* estimates of the probable accuracy of various types of approximation to be made. (In Chapter VI, it is shown that illuminating conclusions can be drawn by "trying-out" approximate methods on models whose exact consequences are already known.) We now show how an approximate computation of the distribution function can be made, the natural mathematical tool being the formation of integral equations. Besides the distribution function as defined above, we can define a whole set of others, e.g. $g_1(\mathbf{x}_1)$ which measures

the probability, subject to a suitable normalising convention, that molecule 1 will be found in an elementary volume surrounding the point defined by the end of the vector $\mathbf{x}_1$, $g_2(\mathbf{x}_1, \mathbf{x}_2)$ defining the probability that molecules 1 and 2 will be found simultaneously near points defined by the vectors $\mathbf{x}_1$, $\mathbf{x}_2$, while $g_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$ is defined in an analogous way. g_1 is, for a liquid, a constant (provided $\mathbf{x}_1$ ends within the volume occupied by the liquid), $g_2(\mathbf{x}_1, \mathbf{x}_2)$ is a function of $|\mathbf{x}_1-\mathbf{x}_2|$ only (as long as the interactions are independent of angle, i.e. are central forces) and is, to a factor, identical with the $g(r)$ we have already defined above. These functions obey various obvious normalisation relationships, e.g.

$$g_2(\mathbf{x}_1, \mathbf{x}_2)=\frac{1}{V}\iiint g_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)\mathrm{d}\mathbf{x}_3 \qquad (2)$$

It is possible to derive recurrence relations between these quantities as follows: We suppose molecule 2 shifted an infinitesmal distance, molecule 1 being held fixed. Then, if the g's take their equilibrium values, this shift can result in no change in the free energy of the liquid as a whole, that is:

$$0=\delta\mathbf{x}_2\left\{-kT\frac{\partial}{\partial\mathbf{x}_2}(\log g_2(\mathbf{x}_1, \mathbf{x}_2))+g_2(\mathbf{x}_1, \mathbf{x}_2)\frac{\partial\epsilon_{1,2}}{\partial\mathbf{x}_2}+\right.$$
$$\left.\iiint g_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)\frac{\partial\epsilon_{2,3}}{\partial\mathbf{x}_2}\mathrm{d}\mathbf{x}_3\right\} \qquad (3)$$

where $\epsilon_{1,2}$, $\epsilon_{2,3}$ represent the interactions between atoms 1 and 2 and 2 and 3 as functions of $\mathbf{x}_1$, $\mathbf{x}_2$, $\mathbf{x}_3$. In this expression, the first term represents the *entropy* change associated with the change in the probability $g_2(\mathbf{x}_1, \mathbf{x}_2)$ of finding molecules 1 and 2 at the distance $|\mathbf{x}_1-\mathbf{x}_2|$ as this distance is varied by altering the position of molecule 2, the second term represents the corresponding change in the average interaction *energy* of molecules 1 and 2, while the integral represents the change in the average interaction energy between molecule 2 and all the other molecules (except 1) (their positions being left unspecified by the function $g_2(\mathbf{x}_1, \mathbf{x}_2)$). Similar equations relate g_3 with g_4, etc., but the set of equations must be *closed* in some way in order to be useful. Equation (3) was actually derived by Born and Green (1947) by a more elaborate argument, but the present derivation seems to bring out more clearly the physical meaning of the various terms. No matter how elaborate a distribution function we use, we seem unable to avoid explicit reference to that for $n+1$ molecules in the course of setting up an equation satisfied by the distribution function for n molecules. So far, the only assumption that has led to a workable theory is the following usually referred to as the "superposition" or Kirkwood approximation:

$$g_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)=\frac{g_2(\mathbf{x}_1, \mathbf{x}_2)g_2(\mathbf{x}_1, \mathbf{x}_3)g_2(\mathbf{x}_2, \mathbf{x}_3)}{g_1(\mathbf{x}_1)g_2(\mathbf{x}_2)g_3(\mathbf{x}_3)} \quad (4)$$

If (4) is inserted into (3) and account is taken of the fact that the forces are central, it is possible to convert this into a true integral equation, as was done by Born and Green (1947).

$$\log\left\{\frac{g_2(r)}{{g_1}^2}\right\}+\frac{\epsilon(r)}{kT}=\frac{\pi}{{g_1}^3}\int_0^\infty\int_{-s}^{s}(s^2-t^2)\frac{t+r}{r}\{g_2(t+r)-{g_1}^2\}\mathrm{d}t g_2(s)\frac{\phi'(s)}{kT}\mathrm{d}s \quad (5)$$

If we treat the departure of g_2 from its mean value ${g_1}^2$ as small we obtain (Rodriguez 1949), after putting

$$\frac{g_2(r)}{{g_1}^2}=\exp\left\{-\frac{\phi(r)}{kT}+\mathrm{f}(r)\right\} \quad (6)$$

$$r\mathrm{f}(r)\approx 2\pi g_1\int_0^\infty\int_{-s}^{s}(t+r)\{\mathrm{f}(t+r)+\epsilon\alpha(t+r)\}\mathrm{d}t\epsilon\alpha(s)s\mathrm{d}s \quad (7)$$

with

$$\alpha(r)=\exp\left(-\phi(r)/kT\right)-1, \quad \epsilon\approx 1+\{\text{average value of } \mathrm{f}(r) \text{ for } r\approx 0\}$$

Kirkwood and Boggs (1942) obtained a somewhat different equation. For a comparison of the consequences of this equation with those of equation (5), the reader is referred to a paper by Kirkwood, Maun and Alder (1951).

Kirkwood and Boggs (1952) began by first deriving an equation analogous to (3) assuming, instead of a slight *displacement* of one specified molecule, an imaginary change in the *strength* of the interaction energy between this molecule and the others. Again, it is possible, by the use of approximation (4), to convert the resulting integro-differential equation into a true integral equation. The reader is referred to the original papers for the detailed derivation of these equations. (It is not altogether clear why the equations of Kirkwood *et al.* and Born and Green are not equivalent to one another, but they both depend on the inexact assumption (4), and it *is* logically possible for two conclusions drawn from the same false assumption by two distinct arguments to be themselves formally inconsistent.) For the present, we accept the fact that both of these equations are approximations, but, nevertheless, they seem to contain within themselves the germ of a combined theory of fusion and evaporation. The first realisation that a type of theory based on the distribution function might cover the solid as well as the gaseous state seems to have been due to Kirkwood (1939). We shall first outline the ways in which the present theory describes the two changes of state, and we shall then review the question of the probable accuracy of any theory based on equations such as (5)–(7).

If we look at equation (7), we see that it is of inhomogeneous

Fredholm type, whose properties are known. Such an equation may be regarded as the limit of a set of inhomogeneous linear equations involving a very large number of variables. Now such a set of equations ordinarily has a unique solution unless the determinant of the coefficients of the variables vanishes. If this determinant *does* vanish, the set of inhomogeneous equations either has infinitely many solutions or none at all. The corresponding result for the integral equation is that, for a certain critical value of the density, the analytical form of the solution changes from one for which $g(r) \to$ constant as $r \to \infty$ to one that can remain periodic even if r becomes large. This is presumed to correspond to the appearance of the solid state. A similar result was obtained by Kirkwood and Monroe (1941), who integrated an equation resembling (7) numerically and reached a precisely similar conclusion, namely that distribution functions of the "liquid" type, for which g_2 approaches a constant value at large distances from a specified molecule, can only be obtained if the density is below a certain value.

A further examination of equation (7) has been carried out by Born and Green (1947) and by Rodriguez (1949). Solving equation (7) by Fourier transforms, they obtain

$$rf(r)=\frac{1}{(2\pi)^{1/2}}\int_{-\infty}^{+\infty}\frac{\epsilon^2 s\beta^2(s)\sin(rs)\mathrm{d}s}{\lambda-\epsilon\beta(s)} \tag{8}$$

where $\lambda=\dfrac{1}{(2\pi)^{3/2}}g_1$

$$r\beta(r)=\frac{1}{(2\pi)^{1/2}}\int_{-\infty}^{+\infty}s\alpha(s)\sin(rs)\mathrm{d}s$$

$$\alpha(r)=\mathrm{e}^{-\epsilon(r)/kT}-1$$

and the analytic form of this solution may be expected to change whenever a pair of zeros of the denominator of equation (8) change from conjugate complex to real. The density for which *real* zeros of this denominator first appear is interpreted by Born and Green (1947) as the lowest density at which the liquid can exist in a metastable state without vaporising. Scoins (1952) has pointed out a technical error in the above treatment, the distribution function following from equation (7) really containing an extra term, this term being of a form which implies *infinite* density fluctuations as soon as the above real zeros appear. This term may possibly be connected with the large density fluctuations that do occur in a liquid near the critical point, and it seems not unreasonable to hope that this term will take a physically more reasonable form in a more accurate theory. We thus have clear indications that the assumption of an interaction energy of the usual attractive-repulsive type has, as logical consequences, a change in the analytic form of $g(r)$ at a certain density and the appearance of truly periodic solutions for $g(r)$ at a somewhat higher density. (The question of which is actually

the *stable* solution at any given temperature and density at which more than one solution is possible has ultimately to be decided by thermodynamic means, as usual.)

It remains to be seen how much further the theory will develop along these lines. The technical difficulties of solving non-linear integral equations, or of determining the analytic form of their solutions, are considerable, but the results outlined above indicate that this approach to a unified treatment is promising. Later on, we shall indicate the connection between theories of this type and the Mayer type of theory. Meanwhile, it is useful to review the evidence at present available on the reliability of the various approximations described above.

The most important of these is the "Kirkwood" approximation (4). Since this assumption does not, in general, satisfy the normalising condition (2), it clearly can be exact only in special cases. Since its physical meaning is far from obvious, it is difficult to set numerical limits to the errors introduced by it, but the following definite statements *can* be made:

(a) It is exact in the limiting case of vanishing low density. For, in this case, two given molecules will only rarely be found near one another, and the encounters 1-2, 1-3 and 2-3 can safely be considered to be *independent* events, the simultaneous happening of all three of which is necessary in order that all three molecules shall be found near one another. Put in another way, if three-molecule encounters are rare, the probability of finding molecules 1 and 2 within a certain distance of one another is practically independent of the position of molecule 3.

(b) Rodriguez (1949) quotes, without proof, the result that the Kirkwood approximation (4) is exact for the "ideal" solid, in which the molecules are so *tightly* bound to lattice points that the energy associated with their displacements can be described by means of Hooke's law. He argues from this and (a) that approximation (4) should be workable for the whole liquid range. This argument is plausible, but not conclusive. One *could* argue almost equally well that the *failure* of such approximations as this might be one of the characteristic ways in which liquids differ from solids and gases.

(c) Rushbrooke and Scoins (1951) have examined separately the effects of the Kirkwood approximation (4) itself, and of the linearising approximation involved in replacing (5) by (6). This they do by comparing the predicted equations of state of the gas of non-interacting rigid spheres that follow from equations (5) and (6) with the accurately known values of the first four virial coefficients for this model. Their conclusion is that B and C, the second and third virial coefficients, are predicted correctly as a consequence of either equation, but that D is not, and the further error introduced by linearising the equation after

making approximation (4) makes one of the contributions to the fourth virial coefficient D negative instead of positive as it should be. Some more general results have been obtained by Rushbrooke and Scoins (1951; 1952; 1953), who show that these approximations have precisely the same consequences as a certain method of approximating to Mayer's (1940) cluster integrals. These results throw only an indirect light on the propriety of using such equations as (6) for a discussion of liquefaction. They certainly show that existing theory is a decent first approximation that can be used in the same sort of semi-quantitative way that the van der Waals theory is used. However, it would certainly seem to be most unwise to use it, as Born and Green (1947) attempted to do, as a way of deciding such subtle questions as the precise analytic behaviour of the partition function in the two-phase region. This, as we shall see below, when discussing Mayer's theory, depends almost entirely on the behaviour of the *high-order* virial coefficients (what is wanted is an indication of the asymptotic variation for large r of the coefficient of v^{-r}), and, since the approximations discussed above in connection with Born and Green's work are already affecting the fourth virial coefficient seriously, it is plain that predictions from equations (6) and (7) about the limiting behaviour of the higher order virial coefficients are, in the present state of affairs, not much more than inspired guesses. (At present there are only very few physical models of a change of state for which the analytic form of the discontinuities is precisely known. See Chapter I, p. 2.) Attempts have been made to derive sets of integral equations without the use of the Kirkwood approximation, Mayer and Montroll (1941), Kirkwood and Salzburg (unpublished), but no method of solving such equations is yet known.

4.3. The "Imperfect Gas" Type of Theory

We have already noticed that the van der Waals type of theory, based on an equation of the same nature as (1), has had considerable successes. The theory itself has been outlined in textbooks often enough to make its detailed development here unnecessary, but there are quite a number of points that call for comment. We know that a simple equation such as that of van der Waals or Dieterici is unable to reproduce all experimental results quantitatively, but it is pertinent to enquire why such equations have had such noteworthy qualitative successes.

The first point of some importance is the justification of the "rule of equal areas", i.e. the rule that, in fig. 4, lines such as EGI, representing the two-phase region, are to be drawn in such a way that the areas EFG and GIH are equal. This rule seems to have been originally formulated by Maxwell, and has been copied by nearly all textbooks. It is usually supported by the entirely fallacious reasoning that, if we performed the cycle of operations indicated by EGIHGFE (fig. 4), the

net work done would have to be zero. If we were to rely on thermodynamics alone, we should have to argue that all these steps can, in principle, be carried out reversibly, so that, since the cycle has been carried out at constant temperature, the net work done has to be zero. This argument certainly cannot be accepted, since the part of the cycle HGF corresponds to a thermodynamically *unstable* region (in contrast with the regions EF and HI which are metastable and therefore can, in principle, be realised). As Fermi points out in his textbook on thermodynamics, it would, apparently, be equally valid to argue that the work done during the hypothetical cycle EFGE should be zero! A better argument is based on the requirement that the partial potentials must be equal at points such as E and I, and we then have

$$0=g_E-g_I=\int_E^I v\mathrm{d}P \tag{9}$$

the integration being carried out at constant temperature. This expression for the change in g as we move about the P-v diagram is valid for a path that links the detached portions DEF and HIJ only on the following condition: The function g associated with one portion is *analytically the same function* as that associated with the other. This does not by any means follow from the ordinary derivations of van der Waals's equation, in which correcting terms for P, given by an improved version of the perfect gas equation, are computed directly, and no attempt at computing either g itself or the corresponding partition function is made. The actual equation of state would not be changed in any way, if, for example, the function representing g on the liquid branch differed by a *constant* (or by some function of the temperature only), from g for the vapour branch, but the rule of equal areas would then be invalid. Such a possibility certainly cannot be excluded by thermodynamics alone. It is necessary to show that there exists a model which leads to the result that g can consistently be represented by *analytically the same function* on both branches of the isothermal. In Section 4.6 (p. 86), we shall show that such a model, which leads to an equation substantially the same as van der Waals's equation, really does exist. We recall that a treatment of a model by statistical mechanics amounts to a direct computation of the partition function, and this, in turn, permits a direct calculation, complete with constants of integration, of the free energy and partial potentials.

The "textbook" derivations of van der Waals's equation lead directly to the equation of state. It is well known, from the theory of the vapour-pressure and chemical constants, that attempts to compute g itself (if the volume and specific heats be supposed given as functions of P and T) can, at best, lead to a knowledge of g subject to a constant of integration. In this situation there is no *a priori* means of deciding

thermodynamically whether this constant is the same for the detached portions of the curve such as DEF and HIJ. (Of course, the integration called for by equation (9) cannot be extended across the two-phase region without begging this question.) Some writers have attempted to avoid this difficulty by connecting points such as E and I by a path that avoids the two-phase region. Such paths, altering the temperature as well as the pressure at each step in such a way as to preserve equilibrium, are readily found, but we now meet a similar question, namely whether the *entropies* of the liquid and vapour phases can be described by *analytic continuations of the same function*—a point that again cannot be settled unless we possess a definite statistical mechanical model. In the model that will be considered in Section 4.6 below such an inference can be made.

Another point that needs discussing is the extent to which van der Waals's and similar equations can be said to be satisfactory reproductions of experimental facts, and the significance to be attached to the fact that they do reproduce many features of both liquid and vapour extraordinarily well, as long as we do not ask for a close quantitative checks. We shall find later, when discussing Mayer's work (Section 4.6), that the equation of state of an imperfect gas can be rigorously expressed by means of the equation

$$\frac{P}{kT}=\frac{1}{v}+\frac{B}{v^2}+\frac{C}{v^3}+\ldots \tag{10}$$

so long as we are outside the two-phase region, and that B, C . . . are quantities that can, in principle, be calculated exactly if the interaction function is supposed to be known. Now, it had, for a long time before Mayer's work, been customary to express the results of experimental work on the equation of state by means of such an equation, the virial coefficients B, C, . . ., being determined empirically to give the best possible fit, and it had become clear that the higher terms in the series (10) often become important long before we approach the liquid region. Why is it, then, that we are able to do so much with equation (1), which is, at best, a mutilated version of equation (10)? (The same could be said of equations such as Dieterici's or Clausius's equations of state.) Before attempting to answer this question, we shall sum up briefly the achievements of an equation such as (1).

(a) The constants a and b deduced in the conventional way from the critical data agree in order of magnitude with those obtained by choosing a and b so as to reproduce approximately the observed values of the first two virial coefficients B and C. Now these coefficients are determined mainly by the behaviour of the gas when departures from perfection are just beginning to become observable, that is under conditions far removed from the critical point.

(b) We have already noted that portions of the curve such as EF and HI (fig. 4) describe respectively a superheated liquid and a supercooled vapour. Temperley (1947) has shown that equation (1) can be used to calculate the maximum temperatures to which a number of liquids can be superheated, agreement with experiment being very satisfactory. Benson and Gerjuoy (1950) have shown that such portions of the curve as III (fig. 4) can be used to describe the behaviour of supercooled vapour, agreement with experiment being moderate. Temperley (1947) has further shown that the region LM (fig. 4) should represent the behaviour of a liquid under tension. Inserting numerical constants he arrived at a theoretical tensile strength for water of the order of 500 atmospheres (the theoretical tensile strength at a given temperature simply being the distance of a point such as M below the volume axis). Since writing the above paper, he has learnt of the botanical work of Ursprung (1915) and Renner (1915), which indicated tensile strengths of cell sap of 300 atmospheres, while L. J. Briggs (1948) has since obtained tensions in water of over 200 atmospheres by a centrifugal method, so that the agreement of theory and experiment is quite as good as one can expect. Berthelot's or Clausius's equations of state make predictions about the metastable regions qualitatively similar to those of van der Waals's equation (so does Dieterici's equation except that it does not predict any tensile strength of liquids). These facts may be concisely summed up by saying that, although van der Waals's and similar equations were originally designed to describe the departure of gases from perfection (and the arguments by which the correcting terms are derived are not even approximately valid for a dense gas or a liquid), they nevertheless provide a satisfactory description not only of the condensation process, but of some of the properties of the liquid state as well.

The explanation of the undoubted fact that equation (1) is approximately valid as an interpolation formula seems to be given by following up an interesting discussion by Mayer, *Statistical Mechanics*, Chap. 13. We have already anticipated his main result, that the virial coefficients B, C, ... in equation (10) can, in principle, all be calculated if the interaction function is known. By a plausible, but not absolutely conclusive, argument Mayer attempts to show that, for an interaction of "attractive-repulsive" type, the virial coefficients should all be positive at high temperatures, that they should all begin by increasing as the temperature falls, but should each pass through a maximum, and should then become zero and then negative as the temperature falls still further. His guess, which is probably correct, is that the temperatures at which these virial coefficients become zero probably all lie between the Boyle temperature (at which B becomes zero) and the critical temperature. At high temperatures the correcting terms are small in any case, while

we expect also an appreciable range of temperatures near the critical point, within which the effects of D and the higher virial coefficients approximately cancel, because they are all changing sign in this region. In this way it seems possible to understand how a simple equation such as (1) can be valid as an approximate interpolation formula over a wide range of temperatures. If the virial coefficients were large and all of one sign (as certainly happens at sufficiently low temperatures) a formula such as (1) might well not be valid at all.

The success of the van der Waals theory means that a fairly crude approach to a theory of a phase-transition may nevertheless turn out to be a valuable first approximation. Experience with other types of transition lends support to this view.

4.4. The "Hole" Theory of Evaporation

The "hole" concept has led to two distinct theories of evaporation as well as to the Lennard-Jones and Devonshire theory of fusion (1939 a, b). Before discussing them, we must distinguish quite clearly between two possible physical meanings of the "hole" concept.

(a) We may think of a liquid as a sort of "debased" crystal lattice which has lost its long-range periodic structure. We try to describe this state of affairs by thinking of a crystal lattice containing a number of vacant lattice points or "holes" and we may suppose further, as in the Lennard-Jones and Devonshire theory of fusion (1939 a, b), that the periodicity of the lattice breaks down when the percentage of "holes" exceeds a certain value, the corresponding displaced molecules occupying *interstitial* positions in the lattice until it becomes completely unstable.

(b) We may fix our attention on a single typical molecule in a liquid and "smooth out" the remainder into a continuum. This typical molecule can be thought of as moving in a "cage" or "cell" surrounded by a fairly high potential barrier (representing the effect of neighbouring molecules) the volume of the cell being approximately V/N, where V is the total volume of the liquid. At any finite temperature there is the possibility of a molecule leaving its "cell," the empty "cell" constituting a "hole" in the liquid, which "hole" will persist until another molecule can jump into it. Thus, we suppose that, at any given instant, there are a certain number of empty "cells" in the liquid, each of a volume slightly greater than that of a molecule. The equilibrium number of such empty "cells" or "holes" will be, in either form of the "hole" concept, proportional to $e^{-U/kT}$ where U is the work that has to be done to create a "hole". If we use the concept in form (b) we can generalise it a little, by allowing the volume, or the equivalent radius, of the "hole" to be variable, so that it may have room for more than one molecule, in which case we need some means of determining U as a function of this equivalent radius r, a point that we shall return to later. If the concept is used

in form (a) it is hardly appropriate to admit the existence of "holes" of varying volume, instead we consider the energy of each molecule removed from the lattice to be U. (If two molecules were removed from two lattice sites close to one another, the energy expended might well differ from $2U$ and one could describe this effect formally by postulating an interaction energy between "holes", depending on their distance apart. The latter refinement of the theory does not seem to have been actually made.)

Before describing how theories of evaporation can be set up, using the "hole" model, it is interesting to see in what way the quantity U is related to other quantities.

(a) In the first place, its order of magnitude could be estimated from the interaction function if this were known. One could estimate the total interaction of the missing molecule with the remaining molecules in the crystal lattice, these being supposed all to be in their places, or one could treat the liquid as a continuum, which would be equivalent to *integrating* the quantity $g(r)r^2V(r)$ over all values of r, $g(r)$ being the distribution function as defined above. In practice, $V(r)$ is known only approximately, even for very simple molecules like the rare gases, so it is natural to look for connections between U and other observable quantities.

(b) The fact that U is the energy required to remove a molecule from the interior of a liquid naturally suggests its connection with latent heat, surface tension and the van der Waals constant a. The two former quantities are related by means of the Laplace theory of capillarity which is based on the assumption of an attractive force of limited range. This assumption is not completely accurate, but can be used provisionally until we are in possession of fairly accurate information about intermolecular forces. We also make the idealisation that the density of the liquid persists unchanged right up to the surface. We omit the steps in the argument, which is given in quite a number of textbooks. (See, for example, Temperley, *Properties of Matter*.) We imagine three basic types of process. First, a typical molecule is taken from the centre of the liquid to a point exactly in the geometrical surface. On the assumption of constant density in each phase and an abrupt jump at the surface, this simply results in halving the number of molecules at any given distance from our typical one. We then consider a typical molecule moved away from the surface to infinity, and compute the work done in removing a whole thin layer of liquid from the surface and carrying this whole layer away to infinity. (The work done in subsequently breaking the layer up into individual molecules is small in comparison.) Lastly, we compute the work done in creating two fresh liquid surfaces. We suppose thin layers of liquid to be successively stripped off the surface, all to be carried away to a great distance, and there reunited

to form a new portion of bulk liquid. We deduce the following formulae:

$$\Psi(z)=-2\pi\frac{\partial}{\partial z}\int_0^\infty\int_0^\infty V\{(z^2+x^2+y^2)^{1/2}\}x\mathrm{d}x\mathrm{d}y \qquad (11)$$

where n is the number of molecules per unit volume, $V(r)$ is the interaction between two molecules and $\Psi(z)$ is the total force on a molecule at a distance z from a flat liquid surface.

$$l=\frac{n}{\rho}\int_{z_0}^\infty \Psi(z)\mathrm{d}z \qquad (12)$$

$$2\sigma=\frac{n}{\rho}\int_{z_0}^\infty z\Psi(z)\mathrm{d}z \qquad (13)$$

where l is the latent heat for unit mass, and σ the surface energy. On the basis of the van der Waals theory, we also derive a connection between l and the van der Waals constant a, which is simply

$$l=a/v \qquad (14)$$

Formula (7) is arrived at on the basis that the correcting term a/v^2 in the pressure is to be attributed to the intermolecular forces. If the molecules are separated to a great distance, the work done against these forces is simply a/v. In the formulae (11)–(14), the processes of separation are imagined to take place at constant temperature. By l we then understand the latent heat measured for isothermal evaporation, similarly by σ we mean the work done in creating unit surface at constant temperature, usually referred to as the surface energy. In equations (12) and (13), the choice of the lower limit z_0 of integration is to a certain extent arbitrary. It obviously cannot be taken as zero, because then the effect of the repulsive part of the field would make the integrals diverge. The most satisfactory convention would be to take it as the "mean distance" between molecules (defined, say, as the cube-root of the mean volume per molecule in the liquid) because we are, in all cases, considering processes in which the separation of molecules is progressively *increased* from this value to infinity. If we regard the molecules as *rigid* spheres, an appropriate lower limit would be $2r_0$, where r_0 is the radius of a molecule.

(c) The quantity U can be estimated from viscosity measurements. Various theories of viscosity have been proposed on the basis of the "hole" model, all of which seem to amount to refinements of the idea that the rate at which a liquid can be sheared is proportional to the number of available "holes", as long as this number is small compared with the total number of molecules present, as will be the case provided we are well below the critical temperature, see, for example, Frenkel, *Kinetic Theory of Liquids*. If we think of the liquid as having a quasi-lattice structure, it will be difficult for molecules to "squeeze past" one

another unless there is an unoccupied lattice site in the neighbourhood. The density of most liquids does not differ greatly from that of the corresponding solids, and this means that the repulsive "cores" of the molecules nearly overlap, so that there would be a strong resistance to shearing forces if "holes" were not present. We are accordingly led to look for a rate of flow proportional to $e^{-U/kT}$, and so for a factor $e^{U/kT}$ in the viscosity. Empirically, we find such a factor and, as in other instances, its effect dominates that of any reasonable power of the temperature. We might expect our formula to contain a factor such as $T^{1/2}$ (which occurs in gas-kinetic theory as a result of the fact that the mean velocity of the atoms, and therefore the rate at which momentum is carried from place to place by a given molecule of gas, also contains such a factor). Now that the interaction functions for a number of simple molecules, such as the rare gases, hydrogen, oxygen and nitrogen, can be taken as fairly well known from analysis of the variation of the second virial coefficient B with temperature, see, for example, Fowler and Guggenheim *Statistical Thermodynamics*, Chap. VII, it might be worth attempting a comparison of observed and theoretical values of a, U, l and σ on the basis of equations such as (4)–(7) (just as the constant $\frac{1}{4}b$ has been compared with various other estimates of the molecular volume, with satisfactory numerical agreement). Such a systematic study does not yet seem to have been made, but there seems no doubt that "order of magnitude agreement" is the least that can be expected.

Now that we have indicated how the energy U, required to create a "hole", can be related to various other properties of the liquid we can see how the concept helps in the setting up of a simple physical picture of a liquid. We first recapitulate the simple yet powerful argument that enabled Eyring (1936) to deduce the law of rectilinear diameters (the empirically observed fact that the mean density of a liquid and the vapour in equilibrium with it is a linear function of temperature). We can infer a remarkable symmetry between the holes in a liquid and the molecules in the vapour in equilibrium with it. We can consider two types of process (a) the removal of a molecule from the liquid, leaving the positions of the remainder unchanged, i.e. creating a hole in the liquid and (b) removing a molecule leaving the density of the liquid constant, i.e. allowing the "hole" to heal up. To a very good approximation the energy expended in the former process is just twice that expended in the latter. This arises simply from the fact that interactions occur between *pairs* of molecules and any two molecules may be thought of as joined by a "bond" (of strength depending on their distance apart), which bond may be thought of as belonging half to each such molecule. The first of the above processes results in breaking all the bonds attached to one molecule and leaving them "unsatisfied",

and each of those bonds attached to the molecule removed corresponds to an exactly similar bond associated with the "hole". If we allow the "hole" to heal up, the latter bonds are satisfied and we regain just half the energy associated with the removal of the molecule and the creation of the "hole". We can thus consistently suppose that the energies required to create a "hole" without removing a molecule from the liquid, and to remove a molecule from the liquid, leaving no "hole", are equal. Further, the entropy of the molecules in unit volume of the vapour will be nearly the same as the entropy associated with the same number of "holes" per unit volume in the liquid, because any configuration of molecules in a given volume of vapour can be duplicated by an equivalent configuration of the same number of "holes" in an equal volume of liquid. Thus, we conclude that the free energy change associated with evaporating a certain number of molecules is equal to that associated with creating a corresponding number of "holes", provided that the numbers per unit volume are the same. Since the "holes" have no mass, this result simply means that the densities of liquid and vapour phases in equilibrium should have a constant sum. Of course, the symmetry is not perfect; no property of a "hole" corresponds to the internal and translational degrees of freedom of the molecule, nor are the small interactions between molecules in the vapour phase duplicated by interactions between "holes". In practice, this means that the entropy associated with one molecule of vapour will be somewhat greater than that associated with a "hole", and this is probably the explanation of the experimental fact that the rectilinear diameter is inclined to the temperature axis. (The simple van der Waals theory also predicts a constant sum for the densities of the two phases, but only in the immediate neighbourhood of the critical point.) Hildebrand and Scott, *Solubility of Non-electrolytes*, Chap. 2, have, however, pointed out that further deductions from this assumption of symmetry between molecules and "holes" do *not* agree well with observed facts.

A more elaborate use of the "hole" concept has been made by Fürth (1941), who introduced the idea that the "hole" may have a variable radius. He supposes the potential energy of the "hole" to be given by the surface energy of the liquid multiplied by the surface area of the "hole", together with the work done in expanding the "hole" against the pressure in the liquid, the pressure inside the "hole" being taken as the saturated vapour-pressure. The effective kinetic energy associated with the motion of the "hole" through the liquid is obtained on the basis of the concept of "hydrodynamic virtual mass", i.e. the "hole" is treated as an empty cavity moving through a continuous liquid. In this ingenious way, the potential and kinetic energies of the "hole" can be estimated as a function of the radius of the "hole" and the mean value of

this radius can then be computed by the ordinary methods of statistical mechanics. The free energy per "hole" is computed by a treatment analogous to that for a perfect gas, i.e. interactions between "holes" are neglected. The resulting expression for free energy is minimised in order to determine the equilibrium radius of the "hole". The boiling point of the liquid then corresponds to the temperature at which this equilibrium radius becomes very large. Fürth (1941) has made extensive numerical comparisons of this ingenious theory with experiment, but the results can only be described as disappointing, the agreement obtained being no better than the "order of magnitude" agreement given by simple equations of state of van der Waals type. The difficulty is that the equilibrium radius of the "hole" turns out to be comparable with the intermolecular distance and the macroscopic concepts of "surface tension" and "hydrodynamic virtual mass" are only qualitatively applicable to a "hole" of such small dimensions.

4.5. Theories based on the "Cell" Model

These theories, in which a typical liquid molecule is thought of as moving in some "effective field", representing its interactions with other molecules, are of interest in that they provide the simplest possible formal framework for theories of evaporation or fusion. One simply takes one of these models, computes the chemical potential per atom, and compares the expression with that given by some simple model of the solid or vapour, the transition temperature at each pressure being given, as usual, by equating partial potentials. In this way, it is possible to get simple formal descriptions of the two changes of state, but one abandons all hope of showing that they follow as automatic consequences of a given molecular interaction. Indeed, no such result has ever been formally *proved* by any method, and the other sections of this chapter seem to show that extremely elaborate methods will be needed to prove it. A theory of "cell" or "hole" type necessarily involves some adjustable parameters which may not be easy to relate to the interaction function. There is, moreover, a fundamental difficulty of principle associated with the "cell" model that has not yet been resolved.

The problem we refer to is usually known as that of "communal entropy", and arises in this way. In a gas, we think of each molecule as free to wander everywhere in the containing vessel, whereas, in a solid, it is a comparatively rare event for a molecule to migrate from one lattice-point to another (the time-constants associated with diffusion in solids are often of the order of hours and days) and the possibility of such migrations is usually ignored in entropy calculations. For a liquid, it is usual to assume that a given molecule has effective access to all regions of the liquid, but the calculations of Pople (1952) try to show that, for the range of values of the quantity (size of molecule)/(size

of cell) that usually occur in liquids, it would be better to omit the "communal entropy" term, which omission is equivalent to supposing that the probability of finding two molecules in a given "cell" is small. So far, no one seems to have devised any satisfactory way of taking care of the range of densities for which neither type of extreme assumption is accurate. (This region must exist *somewhere* between the solid and gaseous states.) The way in which the communal entropy enters the equations is best illustrated by considering a few different versions of the "cell" model.

It cannot be too strongly emphasised that this notion of "communal entropy" is quite independent of the older question about the *indistinguishability* of molecules. (This latter question has been carefully discussed by Schrödinger, *Statistical Thermodynamics*, and Rushbrooke, *Statistical Mechanics*.) Generally speaking, we must, even in assemblies that can be treated by classical statistics, formulate our expressions for the entropy in such a way that *configurations which differ from one another only by interchanges of like molecules are regarded as the same.* If we fail to make such a proviso (sometimes known as "generalised Boltzmann Counting") we at once encounter difficulties like the famous Gibbs paradox. (If we treat our molecules as distinguishable we apparently gain entropy if we allow two samples of the *same gas* at the same temperature and pressure to diffuse into one another.) For some statistical mechanical calculations, these difficulties do not matter, but it is necessary to use "generalised Boltzmann Counting" if we are considering questions such as the equilibrium between two phases, for which we need to know the partition functions themselves rather than differential coefficients of them.

We now consider some specific liquid models and we are then able to study the communal entropy problem further. For simplicity we shall consider only the case where the molecules have no internal degrees of freedom. (It is always possible to allow for any such degrees of freedom by introducing the appropriate extra factors into the partition function.) As we pointed out in an earlier section (p. 54) in a classical assembly the integration over momenta can be carried out forthwith, irrespective of the form of the interaction function, provided only that the interaction energy is independent of the momenta. Our central problem is thus to approximate to the configurational integral $Q(T)$:

$$Q(T)=\frac{1}{N!}\int_{\ldots 3N\ldots}\int \exp\left(-\sum_{i<j} V_{ij}/kT\right)\mathrm{d}\tau_i \ldots \qquad (15)$$

the volume integrations being taken over all co-ordinates of all the N atoms, the factor $1/N!$ being introduced to ensure that we are using "generalised Boltzmann Counting". In this section we are considering

only models in which interactions are represented by some sort of potential field in which all the molecules are supposed to move. If so, this effective potential field will be the same for all the molecules, and the multiple integral (15) then splits up into the Nth power of a three-fold integral, so that:

$$Q(T) \approx \frac{1}{N!}\left(\int\ldots\int e^{-w/kT}\,dx\,dy\,dz\right)^N \qquad (16)$$

where w is a function of position and represents the effective potential energy of any one molecule, due to its interaction with the others. We shall now describe various approximations to w.

(a) The "free volume" model. Here we suppose that w is positive infinite if our typical molecule is within a certain volume Nb, and vanishes for the remainder of the vessel. This is practically equivalent to the "rigid sphere" model, the finite size of the molecules being taken into account, but their attractions being neglected. (16) then becomes simply

$$Q(T) \approx \frac{N^N}{N!}(v-b)^N \qquad (17)$$

when N is very large $v=V/N$, the volume per molecule. The excluded volume b, per molecule, is not necessarily constant, but may vary with density and a moment's consideration of the manner in which, for example, spheres pack into a box, shows that even for the very simplest geometries, such variation is necessary. This model as it stands is too crude to discuss changes of state, since we have taken no account of the attractions between molecules.

(b) The "smoothed potential" model. We postulate an excluded volume as before, but suppose that, in the remaining volume $V-Nb$ each molecule is moving in a constant negative potential $-N\chi$ which represents the average attraction of all the other molecules and therefore should be proportional to N. This leads to the result, instead of (17):

$$Q(T) \approx \frac{N^N}{N!}(v-b)^N e^{+N\chi/kT} \qquad (18)$$

This model is essentially based on the same assumptions as are used in discussing simple properties of electrons in metals, e.g. photo-electric effect, thermionic emission. Its application to liquids is due to Guggenheim (1932). χ and b obviously both depend on the density, i.e. on v. For a suitable choice of χ and b the model would be equivalent to Dieterici's equation, but it is much more general.

(c) We may improve the model still further if we suppose that w behaves in the following way, arguing from the quasi-crystalline structure of liquids. We suppose that there are N positions, of minimum potential energy $-\chi_0$, and that, as we move away from one of these points, the

potential energy increases as the square of the distance, until we approach the neighbourhood of another position of minimum energy. If the attractive field is sufficiently strong there will be regions of high energy between the positions of low energy (corresponding to the situation in an actual liquid in which a typical molecule constantly encounters the repulsive "cores" of its neighbours), and the partition function can be evaluated exactly. This model has been discussed in great detail by Frenkel, *Kinetic Theory of Liquids*. In this model, there is, formally, no actual "excluded volume" but there are regions of the liquid of high energy where our typical molecule is extremely unlikely to be found, so that our assumed field divides the liquid up into N "cells". (This is the first time, during our process of improving the approximation, that the idea of "cells" has appeared explicitly.) In models (a) and (b) (p. 72) it has been unnecessary to specify the geometrical *form* of the regions from which a typical molecule is supposed to be excluded. (We can, if we wish, postulate a potential field that is constant and equal to $-N\chi$ within cells, between which cells there is a high barrier of finite thickness.) Sometimes models of type (a) or (b) are referred to as "free volume" models, as the derivation of (18) only required us to specify the *total* volume forbidden to a molecule, without making the assumption that the field representing the effect of the other molecules has any particular geometrical structure. In model (c) we can complete the calculation if we make the assumption that the barriers are high. If the energy per molecule as a function of the distance r of the typical molecule from the position of minimum energy is

$$\epsilon(r)=-\chi_0+2\pi^2\nu^2mr^2$$

(ν being the frequency of the harmonic oscillations corresponding to this energy), equation (16) becomes

$$Q(T)=\frac{1}{N!}e^{-N\chi_0/kT}\left(4\pi N\int_0^R r^2dre^{-2\pi^2\nu^2mr^2/kT}\right)^N \qquad (19)$$

where R^3 is the volume of one cell$=V/N$. The factor 4π arises from integrating over the angular co-ordinates while the factor N inside the bracket arises from the fact that our typical molecule may be found in any one of the cells. If, as we have assumed, the potential energy is already large when r reaches a value corresponding to about half the distance between lattice points, the molecule is extremely unlikely to be found in such positions and the upper limit of the integral in (19) can then be taken to be infinite without appreciable error. Equation (19) shows us how we can estimate the communal entropy. For, if we suppose that each molecule is confined to a single cell, instead of being allowed access to the entire volume V, the term inside the bracket in (19) is reduced by a factor N, since we must now integrate over a single cell

only, but, at the same time we must remove the factor $1/N!$ from (19) which was introduced in order to avoid Gibb's paradox. (If each molecule is supposed to be confined to only one cell, the question of interchange of molecules does not arise so that the permutation factor is superfluous.) Thus, the net result is to divide $Q(T)$ by the factor $N^N/N! \approx e^N$, and from this we may estimate the communal entropy to amount to just k per molecule. Exactly the same argument can be applied, if desired, to equations (16)–(18), the correction to $Q(T)$ being a factor e^N in all cases. In equation (16), the integral is to be taken over a single cell, of volume V/N, instead of the entire volume V. (Naturally the correction is meaningless unless we are working with models (a) and (b) in their "cell" form). The above derivation of the communal entropy correction shows that it arises, *not* as a result of a reshuffling of molecules and cells (the use of "generalised Boltzmann counting" prevents this from affecting the entropy), but as a result of a typical molecule being allowed to roam from cell to cell at will. In other words, in one case we allow configurations in which *more than one molecule may simultaneously be present in the same cell*, in the other case we exclude such configurations. In an actual liquid near its freezing point, the repulsive "cores" of the molecules are nearly in contact, and doubly occupied cells are presumably unlikely. The situation near the critical point is less clear. Here Buehler *et al.* (1951) have compared the predictions of the Lennard-Jones–Devonshire cell model with experiment and show that, as we might expect, the agreement with experiment is best at high densities. These workers propose an alternative model in which up to two molecules are allowed inside each cell, which should improve the approximation at lower densities. Pople (1951), on the basis of this model, concluded that the communal entropy should be negligible until the volume of a cell reaches about five times that of the "collision sphere" of a molecule, which will scarcely ever be the case in the liquid region. However, it is an observed fact that fluctuations of density *do* occur over large regions of a liquid near the critical point, and such an occurrence is not described at all by any version of the cell model, which postulates a fixed cell size, and this implies a constant density throughout the liquid. As we have just seen, the prediction of the model of Buehler *et al.* (1951) is that there is *no* significant communal entropy, i.e. that most of the cells are occupied by just one molecule. To take care of the fluctuations in density, one would have to introduce an assumption that the effective volume of the cell varied from point to point in the liquid in conformity with the local density. Such a model could be obtained by supposing the effective volumes of the cells not to be all equal, but to be distributed about a mean value V/N in the manner of Fürth's theory (1941). Pople's argument (1951) only shows that the communal entropy is negligible for the region of densities *for which the model with*

cells of uniform size is a good approximation, but this argument really cannot be used to predict anything definite near the critical point, where it is a known fact that large fluctuations in local density do occur, even though the volume per molecule is a good deal less than five times that of the collision sphere (about 40 times the volume of the repulsive "core"). In short, the cell model is not really suited to the critical regions at least not until something more is known about the communal entropy. By a similar, but more physical, type of argument, Mott and Gurney (1938) had previously come to much the same sort of conclusion, namely that the assumed "communal entropy" correction was almost certainly too large *near the freezing point*, but they were not able to say anything about the region near the critical point.

(d) The Debye model. At first sight it seems that a further improvement of equation (18) is possible, namely one might suppose the possible frequencies associated with the vibration of a molecule in a cell to be *distributed over a frequency spectrum* instead of being concentrated near one fixed value. (Such a model has proved of value in interpreting the properties of liquid helium at low temperatures.) It does not, however, seem to be of any greater value than equation (18) in discussing changes of state, at all events this correction is not worth making until more is known about the communal entropy correction. At high temperatures, the corrections introduced into equation (18) by a quantum mechanical treatment of the oscillator, or by supposing the frequencies to be distributed over a spectrum, are small in any case. Moreover, a Debye or similar treatment requires knowledge of the velocity of propagation of *transverse* as well as of longitudinal sound waves, and it is not known for certain if transverse oscillations can exist in ordinary liquids or, if they do not, how one is to cater for the missing $2N$ degrees of freedom. ($3N$ degrees of freedom for the whole assembly, less N for the longitudinal waves.) (See L. Brillouin (1937) for one suggestion, and Frenkel, *Kinetic Theory of Liquids* on the evidence for the existence of transverse oscillations.)

(e) The Lennard-Jones and Devonshire theory. These workers (1937) devised a simple means for estimating the actual form of the field within a cell. This they did by postulating a quasi-lattice structure, and calculating the average potential produced near a molecule by the potentials of its interaction with its nearest neighbours (twelve for face-centred cubic packing). It is sufficiently accurate, and equally realistic physically, to compute the average potential within the cell when the neighbours take up, with equal probability, all geometrically possible positions on the surface of the sphere bounding the cell. A correction to allow for the effect of more distant neighbours is readily made if desired. We omit the details of the calculation, but the results are of some interest. At high densities, the form of the potential is practically

parabolic, as is assumed in the "harmonic oscillator" (equation (19)), but, as we lower the density or increase the volume of the cell, the potential becomes practically that assumed in the "smoothed potential" model of equation (18), i.e., nearly constant within the cell, but rising rapidly to high values near the walls. Once the form of the average potential is known at any density, it can be inserted in equation (16), the integral can be evaluated numerically and the pressure determined by differentiation of the partition function in the usual way. The result is a set of isotherms qualitatively like those of the van der Waals theory. We refer the reader to Fowler and Guggenheim, *Statistical Thermodynamics*, Chap. VIII, for a detailed account of this model and for a comparison of its consequences with experiment. The numerical agreement certainly seems better than one gets with theories of van der Waals type. As one might expect, this type of theory works best for high densities, for which the question of communal entropy does not arise.

It is not so easy to draw any firm conclusions about the validity of such models as the smoothed potential or harmonic oscillator models (18) and (19). Without a detailed model, such as that of Lennard-Jones and Devonshire (1937), we have no means of predicting *a priori* the variation of the quantities χ, χ_0, ν, with density so we cannot draw a complete isotherm. If we fix the density of the liquid, we can determine a formula for the boiling point by the following steps. We write down the free energy of the liquid by means of the usual formula

$$F = -kT \log Q(T) - \frac{3}{2} NkT \log T \qquad (20)$$

the latter term being, as usual, the contribution of the kinetic energies of the molecules to the free energy, while $Q(T)$ takes care of the interactions. The condition for equilibrium is determined by comparing the partial potential $(\partial F/\partial N)_{V,T}$ of the liquid with that for the vapour phase, which we can treat as a perfect gas without much error. Some of the predictions of this theory, that are not dependent on the unknown variation of the quantities χ, χ_0, and ν with density, have been compared with experiment by Fowler and Guggenheim (*Statistical Thermodynamics*, Chap. VIII), but the quantitative comparisons are not particularly impressive. It can be stated that these theories predict a vapour-pressure curve of the correct analytical form and that they account for the rough constancy, for a number of liquids, of the entropy change associated with boiling (the empirical observation usually known as Trouton's rule). A corresponding theory of *fusion* can be built up on the basis of these crude models of a liquid, the partial potential now being compared with that following from the Einstein or Debye models of the solid, and the comparison with experiment is somewhat more successful. See Fowler and Guggenheim: *Statistical Thermodynamics*, Chap. VIII.

4.6. The Mayer Theory of Liquefaction

This theory makes a systematic attack on the problem of the rigorous calculation of the configurational integral for an imperfect gas, the interaction being supposed given. The equation of state can be expressed in the form of a virial series, the virial coefficients being, in principle, known in terms of the interaction function, and liquefaction is associated with the various singularities that occur in the partition function as the density is progressively increased. There seems absolutely no doubt that this approach is basically sound, but there is still much controversy on exactly how the change of state is associated with the singularities and on what the analytical nature of the singularities actually is. Only the first two or three virial coefficients can be calculated rigorously, and the behaviour of the higher ones has to be either guessed at, or estimated from approximate theories. Unfortunately, the very nature of the singularity is itself determined by the limiting behaviour of the higher virial coefficients and our experience in other fields (e.g. ferromagnetism, order-disorder in alloys—see Chapter VI) shows that even fairly good approximations to partition functions can be most misleading when one enquires into questions of this kind. (We remind the reader that when we speak of "singularities", limiting behaviour, etc., we are referring, as always, to an infinitely large assembly.) Determining this limiting behaviour involves a double-limit problem, the volume and the number of atoms both being allowed to become infinite. Since it is only when a series converges absolutely that we can without question alter the order in which such limiting processes are taken, and since what we are studying are series that "only just" converge, it is clear that the passage to the limit requires care. Indeed Katsura and Fujita (1952) have called attention to this point by producing a set of functions, which "mimic" quite plausibly the behaviour expected for an actual set of virial coefficients, and for which the method of taking the limits *is* of importance. Temperley (1954) has considered an idealised type of interaction, for which all the virial coefficients can be calculated explicitly and here again the physical consequences of the model are affected by the manner in which we proceed to the limit of a large assembly.

We shall confine ourselves to classical assemblies, so that our problem reduces to the calculation of the configurational integral $Q(T)$. Quantum corrections are certainly becoming important for some liquids with light molecules and various methods have been evolved by which such corrections to the first few virial coefficients can be computed, but these throw little light on the behaviour of the higher virial coefficients.

We now give a brief outline of Mayer's work. Most of the ordinary methods of statistical mechanics fail as we approach the critical region, because some of the virial coefficients are becoming negative,

and, as a result, some of the standard devices of statistical mechanics, such as replacing a series by its maximum term, become invalid. We can either use one of these simpler methods to obtain the correct formal results for the slightly imperfect gas and assume that these can be extrapolated to the critical region, or we may use the very elaborate mathematics of Born and Fuchs (1938), which enable these formal results to be proved rigorously for the whole vapour region. The reader is referred to Mayer and Mayer, *Statistical Mechanics*, for an account of this method. (The double limit problem mentioned above is not discussed there, but this does not cause trouble until Mayer's series fail to converge, which is, probably, not before we actually enter the liquid region.)

Our problem is to calculate the configurational integral

$$Q(T)=\frac{1}{N!}\int\ldots\int e^{-V/kT}d\tau_1\ldots d\tau_2 \qquad (21)$$

We suppose, as usual, that V can be split up into a sum of pair-wise interactions $V=\Sigma V_{ij}$. (It is usual to suppose that V_{ij} is a function only of the distance r_{ij}, but this is not necessary for the formal development of the theory. V_{ij} is small unless molecules i and j are close together.) Mayer now expresses $e^{-V/kT}$ as:

$$e^{-V/kT}=\prod_{ij}(1+f_{ij}) \qquad (22)$$

where $f_{ij}=e^{-V_{ij}/kT}-1$ and therefore vanishes unless molecules i and j are close to one another. Mayer then imagines the product (22) expanded and classifies the various terms of the product. Some sample terms are given below:

$$f_{1,2}\,,\quad f_{1,2}f_{2,3}\,,\quad f_{1,2}f_{3,4}\,,\quad f_{1,2}f_{2,3}f_{1,3}$$

Consider the term $f_{1,2}f_{2,3}$. This depends only on the co-ordinates of the molecules 1, 2 and 3 and the results of the integration over the co-ordinates of the remaining molecules (4 up to N) simply introduces a factor V^{N-3}, where V is the volume of the vessel. Because of the fact that the molecules are alike, two terms such as $f_{1,2}f_{2,3}$ and $f_{3,4}f_{4,5}$ make exactly the same contribution to $Q(T)$ when the integrations have been performed. Furthermore, the result of integrating a term such as $f_{1,2}f_{2,3}f_{4,5}$ over the co-ordinates of molecules 1 to 5 can be factored into two integrals, because the sets (1, 2, 3) and (4, 5) have no common member. It then follows that a great many of the terms in (22) can, after integration, be factored into powers and products of simpler integrals, the process of factoring stops only when we reach terms such as $f_{1,2}f_{2,3}$ in which every f has at least one suffix in common with another f in the group. Such a group is known as a *cluster* and we define *cluster integrals* in terms of the results of integrating over the co-ordinates of all molecules in the group.

Thus:

$$b_2=\frac{1}{2!V}\int_{\ldots}\int f_{1,2}\mathrm{d}\tau_1\mathrm{d}\tau_2$$

$$b_3=\frac{1}{3!V}\int_{\ldots}\int[f_{1,2}f_{1,3}+f_{1,2}f_{2,3}+f_{1,3}f_{2,3}+f_{1,2}f_{1,3}f_{2,3}]\mathrm{d}\tau_1\mathrm{d}\tau_2\mathrm{d}\tau_3 \quad (23)$$

etc.

The initial factors are just introduced for mathematical convenience. The four terms in the integral for b_3 correspond to the four topologically distinct ways in which three points can be connected up by lines joining them (see fig. 9), and the higher cluster integrals are arrived at on the same principle. Each of the terms in the expanded expression (22) corresponds to just one possible way of drawing lines between N points, each line corresponding to an f factor, and connecting just two points. Thus, if the factor $f_{2,3}$ is present in a term, the points 2 and 3 will be connected in the corresponding diagram by a line, if this factor is absent, there will be no such line in the diagram. Mayer's technique is to group together in b_3 all possible ways of connecting three points, and the value of such an integral is obviously just the same for any set of three atoms. Thus, we do not need to consider all diagrams separately. For to any diagram involving the term $f_{1,2}f_{1,3}$ (say) there will always correspond three others, in which the remaining $N-3$ points, other than 1, 2, 3, are connected up in exactly the same way, but for which we have,

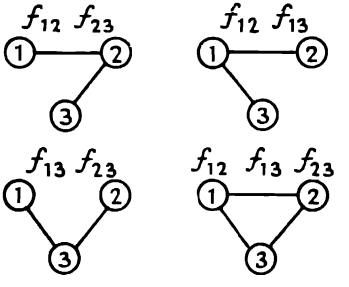

Fig. 9. Illustrating the terms of b_3.

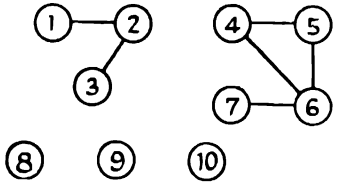

Fig. 10. One of the possible diagrams described by b_3, b_4, $b_1{}^3$.

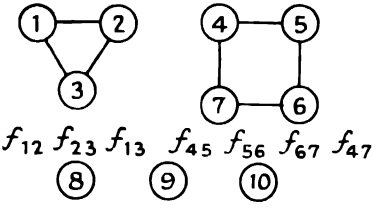

Fig. 11. Another diagram described by b_3, b_4, $b_1{}^3$.

instead of $f_{1,2}f_{1,3}$, one of the other terms occurring in expression (23) such as $f_{1,2}f_{2,3}$. Suppose now, as an example, we consider a diagram in which atoms (1, 2, 3) are connected and in which (4, 5, 6, 7) are also connected. Two possibilities are shown in figs. 10 and 11. The various

other diagrams, corresponding to all the other possible ways of connecting up the first three atoms with one another, and the next four with one another, can also be grouped together with this one. In the general case, any given diagram can be grouped with others in this way until we have used up all the lines in it, and are left with a group of diagrams all agreeing with the following specification: m_1 single points, m_2 pairs, m_3 groups of three connected in all possible ways, m_4 connected groups of four points, and so on, and it is not difficult to see that such a grouping of diagrams covers all possible types of case. When we perform the integrations over the co-ordinates of the corresponding atoms such a group would give us the following contribution to $Q(T)$

$$(b_2V.2!)^{m_2}(b_3V.3!)^{m_3}(b_4V.4!)^{m_4}\ldots \quad \text{or} \quad \prod_l (b_lV.l!)^{m_l}$$

and, if there are m_1 single atoms not connected to any others, integration over their co-ordinates simply introduces a factor V^{m_1}, which we may suppose included in the above product if we *define* b_1 as being equal to 1. The number of possible terms corresponding to each possible choice of the numbers m_l (which must be chosen so that $\Sigma lm_l=N$) is equal to the numbers of ways of selecting, from N atoms, m_1 singlets, m_2 pairs, m_3 triplets and so on, permutations of atoms *within* pairs, triplets, etc., not being allowed. This number is

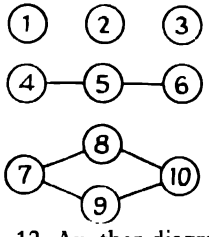

Fig. 12. Another diagram described by b_3, b_4, $b_1{}^3$.

$$N!/m_1!(m_2!)^2(2!)^{m_2}.(m_3!)^3(3!)^{m_3}\ldots(m_1+2m_2+3m_3+\ldots=N)$$

the second factors in the denominator being introduced to remove permutations of atoms within a cluster, which leads to no fresh terms. Multiplying this factor by $\prod_l (Vb_l.l!)^{m_l}$, we obtain the result

$$\frac{Q(T)}{N!}=\sum_{\Sigma lm_l=N}\prod_l\frac{(Nvb_l)^{m_l}}{m_l!} \tag{24}$$

where $v=V/N$ and the summation is to be taken over all possible choices of the m_l's subject to the auxiliary condition $\sum_l lm_l=N$.

The reader who is familar with the theory of permutation cycles may prefer the following treatment. Any permutation of N objects may be represented by a set of *cycles*, e.g. (1, 2, 3) (4, 5, 6, 7) (8) (9) (10) corresponds to the permutation: (1→2, 2→3, 3→1, 4→5, 5→6, 6→7, 7→1). No two cycles may overlap. The different permutations can be grouped into *types*, two permutations of the same type containing the same total numbers of cycles of each length. (We reckon as the same two cycles like (4, 5, 6, 7) and (4, 7, 5, 6) which are usually

counted separately.) The enumeration of terms in (22) after integration can then be summed up as follows:

(a) All diagrams corresponding to the same permutation are to be grouped together. Thus figs. 10 and 11 would be grouped together. When *all* such diagrams have been collected together, the contribution to (24) will be just $(b_3V.3!)(b_4V.4!)b_1{}^3V^3$ from this one permutation.

(b) The contributions to (24) associated with two permutations of the same type are identical. Thus figs. 11 and 12 belong to *different* permutations which make the same contribution to (24), because they belong to the same *type*.

Our problem thus reduces to the enumeration of *all* permutations of a given type subject to the convention mentioned above.

A summation such as (24), to be carried out under an auxiliary condition, is a familiar type of problem in statistical mechanics. $Q(T)$ can be evaluated asymptotically, as long as all the b_l's are positive, by means of the familiar technique of selecting the values of the m_l's which give the maximum term in the series. Using the method of undetermined multipliers, we find, for the corresponding "most probable" values of the m_l's,

$$\overline{m}_l = Vb_lZ_l \tag{25}$$

where Z is an auxiliary variable satisfying

$$\sum_l Vlb_lZ^l = N \tag{26}$$

The corresponding expression for $Q(T)$ is

$$\log\left(\frac{Q(T)}{N!}\right) = \sum_l Vb_lZ^l - N\log Z \tag{27a}$$

from which, by differentiation, we deduce for the pressure

$$PV = \boldsymbol{k}T\sum_l Vb_lZ^l \tag{27b}$$

and the pressure and other thermodynamic quantities can be calculated from this if the b_l's are known. This crude derivation can be replaced by Born and Fuchs' (1938) method which is valid as long as the series (26)–(27) converge. If some of the b_l's are negative, equation (25) is invalid, but (26) and (27) still hold.

So far, the b_l's have appeared simply as integrals of certain types of term appearing in the product (22). They have, however, a physical interpretation. Since the quantity f_{ij} is zero unless V_{ij} differs from zero, it can only contribute to $Q(T)$ for regions of configuration space for which molecules i and j are close together. Thus, we are led to think of the m_l's as quantities which, for a slightly imperfect gas, measure the mean ***numbers*** of clusters of various sizes in the assembly. Put it another

way, the relative probabilities that a specified molecule will be, by itself, in proximity to just one other molecule, in proximity to just two other molecules, etc., are measured respectively by $\overline{m_1}$, $\overline{2m_2}$, $\overline{3m_3}$ and so on. $\overline{m_2}$, for example, measures the *excess* of the actual number of pairs found in the whole vessel above the number that would occur if m_1 single molecules were distributed in the vessel at random. The words "in proximity" could be given an exact meaning if the interactions between molecules had only a finite range. In this case, $2vb_2Z^2$, for example, would measure the probability that, at a given instant, our specified molecule was within this range of exactly one other molecule, and the various terms in (22) can be so interpreted as being associated with different types of configuration. We have explained this physical interpretation of the cluster integrals and the calculated mean numbers of clusters present in the assembly in order to show the possibility of a connection between the b's and the liquid distribution function. (The simple expression (25) for the $\overline{m_l}$'s actually ceases to be formally valid when we approach the liquid region, and some of the b_l's become negative, but the connection with distribution functions persists as we shall see later. As the temperature decreases, the repulsive forces become more important. Since the $\overline{m_l}$'s each measure *excesses* or *defects* in the actual numbers of clusters above or below what would be expected on the basis of completely random encounters among smaller clusters, it is not unreasonable that some of them become negative when the repulsive forces begin to come into play.)

So far, our results have been based on the purely formal manipulation of multiple integrals and the ordinary methods of statistical mechanics, but we have assumed nothing about the interactions except that they act only between pairs of molecules and that they fall off to zero within a fairly short distance. By exploiting the further fact that interactions depend only on the differences between the co-ordinates of two molecules (in cases that have been studied numerically up till now it has always been assumed that the interaction is just a function of the intermolecular distance) it has been found possible to transform equations (26) and (27) into virial series in ascending powers of the density. Consider, for example, the term $f_{1,2}f_{2,3}$ from (22). This is to be integrated over all possible values of the co-ordinates of molecules 1, 2 and 3. We can, however, transform this multiple integral. We integrate first over the co-ordinates of molecule 3, molecule 2 being taken as origin, then over the co-ordinates of molecule 1, molecule 2 being taken as origin, finally the integration over the co-ordinates of molecule 2 introduces a factor V. (There is an implicit assumption here that the shape of the vessel can be chosen in such a way that no appreciable error is made in the integrals as a result of these transformations of co-ordinates.) However, no similar process is possible for the term

$f_{1,2}f_{2,3}f_{3,1}$ By the above argument it can be seen that the result of integrating $f_{1,2}f_{2,3}$ over the co-ordinates of molecules 1, 2 and 3 can be expressed in terms of the square of the simpler integral of $f_{1,2}$ over the co-ordinates of molecules 1 and 2. We call the cluster integrals that can be factored into simpler integrals in this way "reducible", those that cannot "irreducible" cluster integrals. b_2 itself is irreducible, the next irreducible integral is that arising from integrating the term $f_{1,2}f_{2,3}f_{3,1}$. We define the irreducible cluster integrals as follows. We take $k+1$ molecules, write down all possible products involving the f's corresponding to pairs of these molecules and from these select only those terms in which every molecule is linked to every other, directly or indirectly by *more than one path*. If there are two parts of a cluster with only one molecule in common, e.g. $f_{1,2}f_{2,3}$, $f_{3,1}f_{1,4}$, the corresponding integral is reducible and can be factored. We integrate these terms corresponding to irreducible clusters over the co-ordinates of the $k+1$ molecules, divide by $V.k!$ and call the result β_k. (Note that b_l refers to l molecules, but β_k to $k+1$ molecules.) The first few relations between the b's and β's are readily written down, e.g.

$$b_2=\tfrac{1}{2}\beta_1, \quad b_3=\tfrac{1}{3}\beta_2+\tfrac{1}{2}\beta_1^2 \ldots$$

but the general relation between them is a difficult combinatorial problem. For its solution the reader is referred to Mayer's (1940) book. It is found that

$$l^2 b_l=\sum_{n_k} \prod_k \frac{(l\beta_k)^{n_k}}{n_k!} \tag{28}$$

the summation being subject to the condition $\Sigma k n_k=l-1$. Using this relation, it is possible to express relations (26) and (27) in terms of the β's. We shall not carry out the detailed derivations, because the usual methods of statistical mechanics become useless for negative β's while the correct derivation is long and complicated and is given in detail in Mayer's book. We find that

$$\log\left(\frac{Q(T)}{N!}\right)=\log v+\sum_k \frac{\beta_k v^{-k}}{k+1} \tag{29}$$

$$\frac{P}{kT}=\frac{1}{v}-\sum_k \frac{k}{k+1}\beta_k v^{-k-1} \tag{30}$$

$$Z=\frac{1}{v}\exp\left(-\sum_k \beta_k v^{-k}\right) \tag{31}$$

Equations (29)–(31) express the same results as (26) and (27) but in the form of a virial series, the variable Z having been eliminated. (This variable is actually, to a factor depending on the definition, the *fugacity* that appears in chemical thermodynamics and, for slightly

imperfect gases, reduces simply to $1/v$.) Equation (31) is actually the result of reverting series (26), and is an *exact* result as long as both series converge. Thus, it can be stated that the thermodynamic properties of an imperfect gas are known in terms of the β's, for which explicit expressions as definite integrals can be given. So far, only the second and third virial coefficients have actually been evaluated and compared with experiment, thus, as we have seen, enabling valuable evidence to be obtained about the interaction functions. Here we are concerned with the relationship of Mayer's series to the process of liquefaction. The derivation shows that the series (29) and (30) should be valid as long as they are convergent, but it by no means follows that, at any given temperature, two series such as (31) and (27) will break down at the same values of Z or v, even though they may be algebraically equivalent. (As a simple example, consider the algebraically equivalent relations $y=\tan x$ and $x=\tan^{-1} y$. If expressed as series, the first of these relations is valid up to $x=\pi/2$, the second only as far as $x=\pi/4$.) Evidently various types of behaviour are, in principle, possible, depending upon which of the two series (26) or (29) breaks down first as we increase the density progressively, and it even seems possible that the answer to this question may be different at different temperatures. Most workers have supposed, on grounds that are not always clear, that the series (26) breaks down first. We shall also make this assumption and it is possible to produce a simple model (p. 131) for which this assumption is true. It seems clear that the divergence of series (26) corresponds to liquefaction for the following reason. We recall the interpretation of the term $lvb_l Z^l$ as a rough measure of the fraction of molecules to be found in clusters of size l. If Z is "just below" the value at which series (28) diverges, this simply means that the terms with l large are contributing more to N than are those with l small, in other words a given molecule spends a large proportion of its time as a member of large clusters, that is to say, it is in close contact with a large number of other molecules. This is just what is required to explain liquefaction. For, if Z takes the value for which series (26) is "just about to" diverge, a very small change in Z, V being held constant, causes a large change in N, nearly all of which is contributed by the terms of high index at the "top end" of the series, that is, the number of molecules in the "large" clusters increases rapidly. However, equation (27b) shows that the addition of a few large clusters to the assembly would have very little effect on the pressure P. For a nearly perfect gas, we have shown that P is equal to kT/V times $\Sigma\overline{m_l}$, that is, P is proportional to the total mean number of clusters present. Thus, the addition of a large cluster to the assembly affects N far more than P. This suggests that the divergence of series (26) heralds the appearance of a "condensed" phase, and the addition of further molecules then

has no appreciable effect on the pressure. This is just what is required to describe the condensation isotherm, the vapour phase being described by a pressure that increases with increasing density and the two-phase region by a pressure that stays constant if more molecules are added. The temperature at which the divergence of series (26) first becomes possible is then interpreted as the critical temperature. As we have explained above (p. 42) a theory of this kind, in which we average over all accessible regions of phase space, cannot be expected to deal with *metastable* states such as supercooled vapour. This theory gives no explicit treatment of the liquid phase. We can extend it formally to the liquid region by increasing N/V, keeping Z "just below" the value at which (26) diverges. If we supposed that all the b_l's were independent of density, then we should arrive at the theoretical prediction that the pressure was constant for the whole range of values of density above that at which liquefaction began, in other words that the density of the liquid phase was infinite. However, if we suppose that the higher b_l's are *density dependent* (as is mathematically reasonable for a cluster whose physical size approaches that of the vessel itself), we can make the theory predict a liquid phase of finite density. We now have to consider what physical interpretation is to be given to the possible divergence of series (29). Mayer himself (1940) suggested that the temperature at which this first occurs is a kind of lower critical temperature (probably associated with the first appearance of a finite surface tension between the phases), and brought forward various plausible, but by no means conclusive, arguments in support of this view. This general picture has been accepted as reasonable by other workers, e.g. Fowler and Guggenheim (1939), Kahn and Uhlenbeck (1938), Born and Fuchs (1938), who have made reservations emphasising the provisional nature of the arguments used. Recent work, Schneider and Atack (1952), Temperley (1954), suggests that the assumption of two distinct critical temperatures may be unnecessary.

Recently, however, various other views have been put forward. Born and Green (1947) derive an approximate form of equation (29) from distribution-function theory and argue that the appearance of the liquid phase is associated with the divergence of this series and the subsequent appearance of a branch-point in the partition function. Equation (26) does not enter their theory at all and, according to them, the liquefaction temperature is to be obtained just as in van der Waals's theory by equating partial potentials for the liquid and vapour phases (which are described by the two possible branches of the partition function given by the theory). Zimm (1951) has suggested that the critical temperature is marked by a kind of "stop-point" in equation (29) such that not only $(\partial P/\partial V)_T$ and $(\partial^2 P/\partial V^2)_T$ but all the higher derivatives of P with respect to V are zero there. This view is also

backed by various plausible arguments, and is accepted as reasonable by Mayer (1951).

Some light is thrown on these questions, which are hard to handle because there is almost no *definite* information about the behaviour of the higher b_l's and β_k's, by Yang and Lee (1952) and Temperley (1954). Yang and Lee have taken the model of a two-dimensional ferromagnetic, with nearest-neighbour interactions only, and have shown that the known results can be transcribed to give an exact theory of condensation of an idealised two-dimensional gas. They find that this condensation is associated with the divergence of expression (26) but that there is no trace of any second critical temperature such as would be associated with the divergence of expression (29). Temperley (1954) has considered a model for which the interaction between atoms is constant and attractive until two molecules approach within a certain distance and is then repulsive and large. The β_k's can all be calculated explicitly for this model (which is actually a transcription of the Weiss model of a ferromagnetic) and it is found that *no* divergence of expression (29) occurs at any physically significant density, the critical temperature being associated, as in Yang and Lee's model, with the divergence of the expression corresponding to (26). The volume dependence of the higher b_l's, needed in order to describe a liquid phase of finite density, follows from Temperley's model in a natural way. Zimm's (1951) conjecture is definitely false for this second model, but may or may not be true for the nearest neighbour type of interaction. The equation of state following from Temperley's assumption of extreme long-range interaction is

$$P+\frac{a}{v^2}=-\frac{kT}{b}\log\left(1-\frac{b}{v}\right) \qquad (32)$$

which is an equation practically equivalent to that of van der Waals's. This proves the statement (p. 62) that an equation of van der Waals type can be consistently derived from an idealised model, in such a way that the partition functions for the liquid and vapour branches are analytic continuations of one another. This equation corresponds to equation (29) and converges for all $v>b$. The equation corresponding to (26) however describes the liquefaction according to Mayer's picture, and no metastable states of liquid or vapour are predicted. The reader is referred to the original paper for discussion of the fact that this model necessarily implies variations of the higher b_l's with density and how, in this way, the Mayer and van der Waals descriptions of liquefaction are related to one another (at all events for this special model), due regard being paid to the principles laid down above.

The experimental evidence on behaviour near the critical point is conflicting and unsatisfactory. The classic work by Callendar (1928)

on water showed that the behaviour near the critical point was extremely sensitive to the presence of dissolved air in the water. "Gassy" water behaved qualitatively in the manner predicted by the van der Waals theory, but, if the air was nearly all removed, there seemed to be a finite region of temperature above which there is no meniscus, but still a difference in densitities, and the extrapolated "liquid" and "vapour" lines seem to cut at a sharp angle, a result that is not predicted by any theory. Somewhat similar results have been reported by Maas *et al.* (1933–48). (It is, however, not entirely certain whether these differences in density persist if there is adequate stirring.) We recall (p. 14) that the "thermodynamic driving force" tending to equalise densities in two small volumes near one another is expected to become vanishingly small in this region. Zimm (1950) has studied the critical mixing curve of two liquids by a delicate light scattering experiment intended to reveal the analogous effect of the persistence of two different densities in the region just above the mixing curve, with completely negative results. Hildebrand and Scott, *Solubility of Non-Electrolytes*, give discussion of the various possibilities. They favour the "hypothesis of the derby hat", i.e. the existence of a region in the phase diagram at which a difference in densities is possible although the surface tension is zero.

However, Rice and Rowden (1951; 1952) have studied the system aniline-cyclohexane, taking great precautions to secure purity, and have obtained evidence that part of the critical mixing curve may be accurately flat, but find no real evidence of more than one critical temperature. Schneider and Atack (1951; 1952) have studied the critical regions of the pure substances sulphur hexafluoride and xenon. The latter presumably has a "simple" law of interaction, and they bring forward strong evidence to show that the *apparent* flattening of the peak of the critical curve and the appearance of a gradient of density even above the critical point are merely effects of the pressure-gradient due to gravity (which may be expected to become more and more important as the critical region is approached). Indeed, they show that a calculation based on a critical isotherm of "classical" type, inserting the effect of gravity, can account for a density gradient of the observed order of magnitude. It remains to be seen whether the similar effects found by other observers can be accounted for in this way, or whether the true situation near the critical point really *is* basically more complicated than a van der Waals type of theory would predict. We have already found two idealised models for which Mayer's attempted description of the critical region is incorrect, Temperley (1954), Yang and Lee (1952).

Yet another view of the position has been put forward by Scott (1953), a similar point having previously been made by Price (1951). Scott

points out that if the result following from a theory of van de Waals type for the region below T_c

$$(V_g - V_l)^2 \propto T_c - T$$

were replaced by

$$(V_g - V_l)^3 \propto T_c - T$$

the result would be the correct λ-point type of anomaly in the specific heat. He quotes evidence, Guggenheim (1945), Zimm (1950; 1951), that the suggested cube law may be of fairly general validity. Onsager (unpublished) thinks that this cubic law may be characteristic of three-dimensional assemblies with short-range interactions. (The corresponding result for a two-dimensional gas with nearest neighbour interactions only, Yang and Lee (1952), is an *eighth-power* law, instead of the cube law, and this also seems to be of great generality, holding for several two-dimensional models. It has been shown that it would hold for the plane square, plane triangular and plane honeycomb types of lattice.) For these simple models (and for the plane square lattice with interaction between second nearest neighbours as well as nearest neighbours) it has also been shown, Temperley (1952), that the "boundary tension" (the two-dimensional analogue of surface tension) would be finite everywhere in the two-phase region. The "derby-hat hypothesis" is therefore incorrect for these idealised models, corresponding to the extreme cases of interactions of very short and very long ranges, for which explicit computations are possible, and Schneider and Atack's work (1951; 1952) throws real doubt on the actual reality of the "two-density, no meniscus" region.

We end this section by reviewing briefly the relationship between "clusters" and distribution functions. We have already shown how, if we know the distribution function as a function of density, the virial equation and hence the β_k's are all known. An even more direct connection is given in this way. If we take the configuration integral $Q(T)$, which involves integration of the Boltzmann factor $e^{-V/kT}$ over the co-ordinates of N atoms, but omit one of the integrations, we get a function of the co-ordinates of one molecule which measures the relative probabilities of finding it at various places in the vessel, the other molecules being averaged over all possible positions. Plainly, this function is just a constant except in the presence of external fields. If we omit a second integration, we get a function of the co-ordinates of *two* molecules, the Boltzmann factor representing the total interaction being averaged over all possible positions of all the other atoms. Plainly, this average will only depend on the relative positions of the two molecules and thus measures the relative probability of finding two molecules at a specified distance, i.e. to a factor it is the two-molecule distribution function

$g_2(\mathbf{x}_1, \mathbf{x}_2)$. The omission of further integrations leads similarly to the distribution functions of higher order. We can derive various other functions by omitting one or more of the integrations in the cluster-integrals. The reader is referred to two papers by Mayer and Montroll (1941) in which this point of view is elaborated in detail, and many relations are obtained between these various types of function. The distribution function theory outlined in Section 4.2 above now emerges as a possible means of by-passing the difficult calculations of $Q(T)$ or the cluster integrals, if some alternative means of computing the distribution function, e.g., as a solution of an integral equation, can be found. Mayer and Montroll (1941) indeed find such integral equations, but do not attempt to solve them.

4.7. Irreversible Effects associated with Evaporation and Liquefaction

We have already alluded to the use of the van der Waals theory for accounting for some of the observed facts on both metastable liquid (superheated) and vapour (supercooled). The reader is referred to papers by Temperley and Chambers (1946) and (1947) and Benson and Gerjuoy (1950) for reviews of the experimental evidence. Further experimental information is given by Ursprung (1915), Renner (1915), Harvey (1944), Scott *et al.* (1948) and L. J. Briggs (1948). Briefly one can sum up the situation by saying that, as usual, the van der Waals type of theory reproduces some of the facts well, others only in order of magnitude. It is, however, quite incorrect to say, as do nearly all the textbooks, that the "theoretical" tensile strength of a liquid obeying the van der Waals equation is given by the tern a/v^2 ($\approx$10,000 atmospheres for water). The "correct" theoretical value for water on the basis of such an equation of state is of the order of 500–1000 atmospheres, compared with the largest experimental values of about 300 atmospheres. Ursprung (1915), Renner (1915), L. J. Briggs (1948).

Various other theories of these effects have been given, almost all of them based on surface tension as the factor which is responsible for the metastable effects. This idea is undoubtedly correct in principle, but the two types of theory are not necessarily in conflict—we have already noticed the close connection (p. 66) between surface energy and the van der Waals constant a. Naturally, there may be expected to be considerable symmetry between theories determining the formation and survival of drops in a supercooled vapour and of vapour bubbles in a superheated liquid. Consider first just a single bubble of vapour of radius r in a liquid and suppose that the pressure in the liquid is less than the equilibrium vapour pressure by an amount P. Then, if σ is the surface energy, the bubble will expand if

$$\frac{\partial}{\partial r}\left(-\frac{4\pi Pr^3}{3}+4\pi r^2\sigma\right)\leqslant 0 \quad \text{or} \quad P\geqslant\frac{2\sigma}{r}$$

so that, to explain the fact that observed tensions in liquids (or supersaturation pressures due to dissolved gases) are not greater than hundreds of atmospheres, we have apparently to account for the permanent presence, in liquids or on their boundaries, of bubbles of radius of the order of 10^{-6} cm. Any bubble smaller than this should be unstable and would be compressed out of existence if it existed in the body of the liquid, though it might survive at the walls. See Frenkel, *Kinetic Theory of Liquids* (1946). It is not possible to account for bubbles as large as this merely by statistical fluctuations. Fürth's theory of "holes" enables the probable radius of the holes to be estimated, and, at ordinary temperatures, it is only of the order of intermolecular distances, as one might expect, leading to predicted tensile strengths of the order of thousands of atmospheres. It is true that there is experimental evidence, Alty (1926), that bubbles of gas in water carry an electric charge. Extrapolating his figures to much smaller radii, it is conceivable that bubbles of the order of 10^{-6} cm radius might (if permanently charged) be stable for long periods against surface tension, but this does not explain their appearance by fluctuations in the first place. There is qualitative evidence, Harvey *et al.* (1944), that nuclei are irreversibly removed from water by pre-application of high pressure, so that it is afterwards capable of standing higher tensions than before, and this fact would be explained if the bubbles lost some of their charge when compressed and did not regain it on expansion. Such behaviour is not unlike some effects observed by Alty (1926). A less serious discrepancy exists for drops in vapour. If l=latent heat/unit mass and σ=surface energy, a drop whose radius was less than the value given by

$$4\pi r^2\sigma=(4/3)\pi r^3\rho l$$

that is

$$r=(3\sigma/\rho l)\approx 5\times 10^{-8} \text{ cm for water}$$

would have sufficient surface energy to evaporate spontaneously, so that a stable drop would have to be at least as big as this. This is still rather unlikely to be formed spontaneously, because quite a number of molecules would have to collide simultaneously, which is an improbable event in the vapour phase.

We are thus led to consider the growth from small beginnings of drops and bubbles as a problem analogous to chemical kinetics. Small drops and bubbles form by statistical fluctuations, and some of these collide to become larger ones. The theory for drops was developed by Becker and Döring (1935) and that for bubbles by Fisher (1948), this type of theory of the kinetics of a phase change usually being referred to as a

"nucleation" theory. Sometimes a phase-change proceeds by the independent growth of small numbers of nuclei, sometimes, as in this case, it seems necessary to estimate the rates of growth, decay and mutual conversion of nuclei of all possible sizes. The striking feature of a theory such as Fisher's (1948) is the great *sensitivity* of the time interval predicted for the disappearance of a metastable state to the extent to which this state departs from equilibrium. Put in the opposite way, the calculated limit of metastability (e.g. applied tension, degree of superheating) is practically *independent* of the time interval we choose as the "time of doing an experiment", provided that we do not actually set this time equal to zero or to infinity. *Any* reasonable choice of time interval leads, for water, to an expected tensile stength of the order of 1000 atmospheres, practically the same as is given by the van der Waals type of theory. It seems fair to say that these two types of theory are complementary, not contradictory. We recall the discussion in Chapter III (p. 38) in which it was shown that a satisfactory microscopic description of irreversible effects could be given (in spite of microscopic reversibility) provided that our statistical averaging processes were carried out over a time that might well be very long, without being mathematically infinite. Fisher's work (1948) seems to show that a satisfactory "plateau time", in Kirkwood's sense (1946), *does* exist for this problem, and this means that a satisfactory statistical mechanical theory of metastable phases should also be possible for the liquid-vapour transition.

The Becker-Döring theory is based on Kelvin's equation (1871) for the vapour pressure over a surface of radius r

$$P_r/P_\infty = \exp(2\sigma m/\rho r k T) \tag{33}$$

where m=mass of a molecule, ρ=density of liquid and σ=surface tension. This equation was originally derived thermodynamically, and has been experimentally checked for small drops by la Mer and Gruen (1952). Becker and Döring consider the growth of drops, e.g. in a cloud chamber, as analogous to an "open" chemical reaction, in which the numbers of drops of various sizes remain constant. The drops that reach a certain size (containing g molecules, say) are supposed to be continuously removed from the assembly, a corresponding amount of material being fed into the assembly in the form of single molecules of vapour. We also neglect processes in which more than one molecule condenses or evaporates from a drop at a time. Thus, a drop containing g molecules may lose a molecule by evaporation, the probability of which we set equal to $\alpha_g S_g$, where α_g is the probability that a molecule will evaporate from unit area of drop in one second and S_g is the surface area of the drop. Similarly we set $\beta_g S_g$ equal to the probability that such a drop will gain another molecule in unit time.

Our idealised process may be thought of as an "assembly-line", molecules evaporating from and condensing on to each drop, but a typical drop gradually grows in size until it reaches the critical size G, when it is removed. Let I be the number of drops of size G removed from 1 cm^3 of the vapour per second, and let g^* be the size of drop that would be in equilibrium at the given pressure of vapour. Let f_g be the number of drops per cubic centimetre of the size g, and we suppose that these numbers remain steady. The number of drops of size g created per cubic centimetre per second.

$$=\beta_{g-1}S_{g-1}f_{g-1}=\beta_{g-1}F_{g-1} \quad \text{(say)}$$

Number of drops of size g reduced to size $g-1$ per cubic centimetre per second

$$=\alpha_g S_g f_g=\alpha_g F_g \quad \text{(say)}$$

Now, to maintain the "assembly-line" process and keep conditions steady, the net number of drops of size G removed from the assembly must be equal to the number of drops of size $G-1$ that grow to size G. That is

$$I=\beta_{G-1}F_{G-1}$$

This number must be supplied by drops growing from size $G-2$ to $G-1$ and we must also replace these of size $G-1$ that lose a molecule by evaporation and decrease to size $G-2$.

Thus

$$I=\beta_{G-2}F_{G-2}-\alpha_{G-1}F_{G-1}$$

Similarly we have

$$I=\beta_{G-3}F_{G-3}-\alpha_{G-2}F_{G-2}$$

$$\cdots \qquad\qquad \cdots$$

$$=\beta_2F_2-\alpha_3F_3$$

$$=\beta_1F_1-\alpha_2F_2$$

Whence

$$\frac{\beta_1F_1}{I}=1+\frac{\alpha_2}{\beta_2}+\frac{\alpha_2\alpha_3}{\beta_2\beta_3}+\cdots+\frac{\alpha_2\alpha_3\cdots\alpha_{G-1}}{\beta_2\beta_3\cdots\beta_{G-1}} \qquad (34)$$

We can estimate β_1F_1 from kinetic theory, if we assume that two molecules of vapour stick together whenever they collide.

The series (34) can be summed approximately if we can form some reasonable estimate of the behaviour of α_g/β_g as a function of g. This ratio clearly >1 for $g<g^*$ and <1 for $g>g^*$, so that, provided G is chosen to be appreciably greater than g^*, the exact choice of G will not matter greatly. Actually, insertion of numerical values shows that

$$\frac{\alpha_2\alpha_3\cdots\alpha_g}{\beta_2\beta_3\cdots\beta_g} \quad \text{has a strong peak at } g=g^*$$

For g large, β_g approaches the gas-kinetic value $P(2\pi mkT)^{-1/2}$ that we should calculate for a flat surface, on the basis that every molecule striking the surface is captured. On this assumption α_g^*, the rate of evaporation from unit area of an equilibrium drop must also take this value. For other sizes of drop we assume α_g to be proportional to the equilibrium vapour-pressure over a drop of size g, which we estimate from (33).

Thus for large g, and r_g being radius of drop of size g,

$$\frac{\alpha_g}{\beta_g}=\frac{\alpha_g}{\alpha_g^*}=\frac{P_g}{P}=\exp\left\{\frac{2\sigma m}{\rho kT}\left(\frac{1}{r_g}-\frac{1}{r_g^{*-1/3}}\right)\right\}$$

$$=\exp\left\{\frac{2\sigma m}{\rho kT}\left(\frac{4\pi\rho}{3m}\right)^{1/3}(g^{-1/3}-g^{*-1/3})\right\} \qquad (35)$$

In default of anything better, we assume this formula for all sizes down to $g=2$. This assumption enables us to make a numerical estimate of the rate of formation of drops, and crude assumptions of this kind have probably to be used in considering other types of nucleation process. On such an assumption, we can evaluate the typical term

$$\frac{\alpha_2\alpha_3\ldots\alpha_g}{\beta_2\beta_3\ldots\beta_g}$$

in the series (34)

$$\frac{\alpha_2\beta_3\ldots\alpha_g}{\beta_2\beta_3\ldots\beta_g}\approx\exp\left[\frac{2\sigma m}{\rho kT}\left(\frac{4\pi\rho}{3m}\right)^{1/3}\left\{\sum_2^g(g^{-1/3})-(g-1)g^{*-1/3}\right\}\right] \qquad (36)$$

The sum $\Sigma g^{-1/3}$ can be replaced by an integral with sufficient accuracy, and then the sum (34) can also be replaced by an integral over g. The integrand is a maximum for $g=g^*$ and we can approximate by the method of steepest descents. We obtain finally

$$I\approx\frac{\beta_1 F_1}{g^*}\left(\frac{A}{3\pi}\right)^{1/2}e^{-A} \qquad (37)$$

where

$$A=\frac{\sigma m}{\rho kT}\left(\frac{4\pi\rho}{3m}\right)^{1/3}g^{*\,2/3}\approx 50 \text{ for water}$$

This equation shows, though in a less extreme form, the behaviour noted by Fisher (1948). We assume a "reasonable" value for I, corresponding to a rate of formation of large drops that is easily observable. From (37) we can estimate the corresponding value of $g^{*\,2/3}$, and from (33) the corresponding value for the "critical supersaturation pressure". It can be seen from these equations that the calculated critical supersaturation pressure is not at all sensitive to the precise value of I assumed, provided of course that we do not assume it to be infinity or zero.

Here again, it seems that we have an assembly that possesses a "plateau time" in Kirkwood's sense (1946), so that we get much the same critical supersaturation pressures on the basis of this crude "kinetic theory" picture as we do by computing the limit of the metastable region according to an equation like that of van der Waals. See Benson and Gerjuoy (1950). For a discussion of possible improvements of the Becker-Döring theory and a comparison with experiment, the reader is referred to Barnard's review paper (1953).

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CHAPTER V

Fusion and Solidification

5.1. Introductory

In the last chapter we referred to the objective of developing a model of the liquid state that should be capable of describing both fusion and evaporation, and it appeared that the only models so far suggested that were, in principle, capable of doing this were the "hole" model and the attempts of Born and Green (1946–7), and of Kirkwood and his pupils (1935–50), to calculate the liquid distribution function by means of an integral equation. The former type of theory necessitates the *ad hoc* introduction of parameters of various kinds in order to describe the numbers and mean size of the holes, e.g. they may be thought of as vacancies in a crystal lattice, Lennard-Jones and Devonshire (1937), or as bubbles in the liquid phase, Fürth (1941). Any such assumptions can, not unfairly, be described as, in a sense, guesses about the nature of the phase-transitions themselves, and thus it would always be possible to criticise such a theory by arguing that no *a priori assumption* about the nature of the mechanism of the phase changes should be made, as the physical features of these transitions ought to be automatic consequences of the interaction. For theories of distribution function type no such criticism can be made. Such theories attempt to predict an equation of state *a priori* from an assumed interaction function, and the phase transitions then, in principle, follow as consequences of changes in the mathematical behaviour of the integral equations whose solution is the distribution function. A two-molecule distribution function can be defined for *any* assembly, so the mere assumption of its existence does not impose any physical restriction on the assembly, while, for example, the assumption that a liquid can be described as a solid lattice with a number of vacancies certainly does imply an *a priori* assumption about the liquid state. If, further, we associate fusion with a singularity in the function specifying the number of "holes", we are introducing another definite assumption. The distribution function type of theory is therefore logically preferable to the other types so far suggested, as it assumes no more than a molecular interaction function as its logical premiss. At present, however, fairly drastic approximations have to be made to enable the mathematics to be carried through at all, so that, at present, there is little to choose between this and other types of theory.

Besides theories of this sort, that attempt to cover the whole liquid

range, there are theories that describe simply the liquid-solid transition (just as there are theories of the van der Waals type that describe only the liquid-vapour transition). These either involve setting up separate models of the liquid and solid phases, or else describe the differences between the two by means of one or more parameters that vary discontinuously with temperature (analogous to the term a/v^2 in van der Waals's equation). In either of these cases, the melting curve is obtained by the usual process of equating partial potentials for the two phases. Finally, there is an even more "primitive" type of theory, which merely attempts to show that at a high enough temperature the solid state is *unstable* with respect to certain types of disturbance in its structure, no attempt being made to set up a model of the liquid state. Such a theory can, at best, give only a qualitative picture of the melting curve, first because, as in all stability problems, there is always the possibility of some disturbance, other than one of the type assumed, leading to instability of the solid at a still lower temperature, secondly because, even if we have found the right degree of freedom (the one that first leads to instability), a *discontinuous jump* to the other phase occurs, in general, *before* the first phase actually becomes unstable against *small* disturbances. (We have already discussed this situation in detail in connection with the van der Waals theory, and the reader will be familiar with the fact that the vapour can change *reversibly* to liquid at a temperature higher than that at which the vapour phase becomes completely unstable.) Such theories as these are, therefore, quite incapable of dealing with any of the finer details of the transition, but they are by no means valueless or out of date. They did give physical insight into the nature of melting at a time when no better theories were available, and they are certainly of value today in suggesting in what ways a solid is most likely to become unstable when heated.

5.2. Attempts to show that the Solid becomes unstable

The earliest theory of this type is due to Lindemann (1910). It was based on the idea, which can be expressed in a number of different ways, that the melting process involves a transition between a state of affairs in which a typical molecule continually vibrates about its position of equilibrium in the lattice and a state of affairs in which the typical molecule only makes a few such oscillations, then collides with one or more neighbours and begins to vibrate about some fresh position of equilibrium. This physical idea is almost certainly correct, but, expressed in this form, quantitative deductions are not easy. One is led to predict the existence of some sort of law of corresponding states, for example, that melting might be expected when the mean amplitude of oscillation of a typical molecule is, for all solids with the same crystal structure, the same fraction of the lattice distance. If we had a solid of

Einstein type (all molecules vibrating about their positions of equilibrium with practically the same frequency), we should expect a result of the following type

$$kT = 4\pi^2 \nu_0^2 m \overline{r^2}$$

where m is the molecular mass, ν_0 the Einstein frequency and $\overline{r^2}$ the mean square displacement of a typical molecule. If we now postulate that melting occurs when $\overline{r}$ is a given fraction of R, the lattice spacing, we should expect that

$$T_m \propto R^2 \nu_0 m \tag{1}$$

where R is related in an obvious way to the molecular volume N/V, R^3 being proportional to V/N, the constant depending on the crystalline type.

It is not, in fact, possible to describe solids by means of a *single* characteristic frequency, but, using the Debye theory of specific heats, we can argue that, to an approximation sufficiently good for a theory of this kind, the spectra of characteristic frequencies of solids differ only by a scaling factor, so that each solid is described by its characteristic Debye frequency ν_D, which frequency we can insert into (1). Since an empirical constant is already involved, this makes no material difference. It is fairly well known that, experimentally, a relation of this kind does hold reasonably for many different solids. Recently, the law has been tested in a slightly different way, Simon and Domb (1952). The melting curve of helium has been traced up to nearly 10,000 atmospheres and, since it is a very compressible solid, there are large changes in the lattice distance and in the Debye ν_D, nevertheless the law (1) holds with good accuracy over the whole range so far investigated. This is a little surprising because, for helium, T_m is always small compared with the Debye temperature Θ, in which circumstances it is not correct to assign an energy of kT_m to each degree of freedom, but one should instead use Planck's expression, so the original argument from which the formula was derived is no longer applicable.

Lindemann's theory in no way *proves* that any lattice becomes unstable, it merely attempts to set up a law of corresponding states, being given the assumption that a rough explanation of melting is to be looked for on the lines just indicated. The first definite attempt to *prove* that a crystal lattice became unstable seems to have been due to Braunbek (1926). He attempted to determine the criterion of stability by discussing a somewhat strange lattice distortion, namely, he imagined the crystal divided into two interlacing sublattices and considered a relative displacement of these two, and assumed the associated restoring force to be a periodic function of the displacement. On this basis he concluded that, for a given temperature, i.e. a given total kinetic energy

of the molecules in the lattice, there might be two possible values of the potential energy, and he proposed to identify the corresponding configurations of the lattice with the solid and liquid states. This must really be regarded as an attempt to prove that the solid lattice is unstable, because the lattice of a solid distorted in this strange fashion seems a highly artificial model for a liquid. Herzfeld and Geoppert-Mayer (1934) calculated the equation of state of a Debye lattice and showed that, at a certain temperature, $\partial P/\partial v$ would become zero and a finite expansion might then be expected, that is *the bulk modulus would vanish*. Raschevsky (1927) also attempted to set up a criterion of this kind. Born (1939) attempted to show that the *shear* modulus of an ideal crystal would vanish at some temperature, an idea that was elaborated by Fürth (1941), who attempted also to show that surface faults would play a decisive rôle as instability approached, and he was led by this to an attempt to correlate the (as it seems to the author) almost completely unrelated phenomena of *melting* and of *breaking under tension*.

A recent example of a theory of the same type is due to Bonfiglioli, Ferro and Montalenti (1952). They represent the force on a typical molecule as $-\alpha x+\beta x^2$, where x is the displacement of the typical molecule from a lattice point. This leads to a progressive change of the mean position of the atom as its energy increases, this being a well-known property of the anharmonic oscillator. Thus, β can be correlated with the thermal expansion of the lattice. The condition of instability corresponding to melting is taken to be, for the mean displacement, $x_m=(1/2)\alpha/\beta$, the physical reason for the choice of the coefficient $1/2$ not being obvious. (A more natural choice would seem to be unity, because then the restoring force vanishes.) On this basis they are able to deduce Gruneisen's law (that the coefficient of expansion is inversely proportional to T_m), and to correlate roughly the melting temperature with α, that is with the compressibility, obtaining a relation practically equivalent to Lindemann's (1910). A comparison of the predictions with experiment gives reasonable numerical agreement, considering the simplicity of the model. Moreover, this model gives a definite physical reason for the instability of the solid lattice, which Lindemann's theory did not do.

About all these theories two things can certainly be said. First, in a system of any degree of complication it is notoriously difficult to "spot" the probable mode of failure. If one guesses wrongly, the result will be to predict too high a melting temperature. In principle, the programme would seem to be to take a very simple lattice, apply each of these theories to it, and see which predicted the lowest melting temperature. However, such a programme is hardly worth while, because, as we have already pointed out above, what is wanted is not the temperature at which the solid becomes *absolutely* unstable against

a small perturbation, but instead the temperature at which it becomes unstable relative to the liquid phase. Therefore, such a theory can be no more than qualitative as long as the stability is studied by means of perturbation techniques (small oscillations). A great deal of work on *non-linear* mechanisms and their stability has been done recently, some of which may well be applicable to this field. Until this is done, the foregoing criticisms must remain valid. In the next section we consider a number of attempts to set up theories of both phases.

5.3. Theories that attempt to describe both Phases

For convenience, we may subdivide this section. We can conceive of a theory resembling van der Waals's in which a single "model" attempts to describe both phases in the neighbourhood of the melting line. Braunbek's theory (1926) could have been put into this class, but his picture of the "liquid" is artificial. The other possible line of attack is to set up *different* models of the two phases, and then to determine the melting line simply by equating partial potentials.

(*a*) *Solid and Liquid represented by one model*

The first theory of this kind was due to Lennard-Jones and Devonshire (1939 a, b). Starting with a perfect crystal lattice, they show that, besides the regular lattice sites, it contains also other interstitial positions, into any of which a molecule can be inserted at a small expenditure of energy. Against this extra energy has to be set the fact that there are many more possible arrangements of the lattice if an appreciable number of molecules occupy such interstitial sites, a corresponding number of lattice sites being left vacant. If there are N lattice sites, N possible interstitial sites and if n molecules are transferred from the lattice to interstitial sites, the number of possible arrangements is $\binom{N}{n}^2$, and we have, as usual, to set the corresponding increase of entropy against the loss of energy. If we assumed that the energy expended in removing a molecule from the lattice to an interstitial site was constant, independent of n, the result would simply be a gradual increase in n as the temperature rose. To explain a *sudden* onset of melting, it is necessary to suppose that this energy expenditure is itself a function of n, so that the theory becomes one of the same type as the van der Waals theory. The simplest assumption that one could make is that, as the lattice becomes less perfect, the energy expended on placing one lattice molecule in an interstitial site decreases linearly as n increases. Such an assumption would indeed lead to a discontinuity —in fact the theory becomes quite analogous to the Bragg-Williams or Bethe theory of order-disorder in alloys (p. 115). Both types of theory were tried by Lennard-Jones and Devonshire (1939 a, b). By itself, such

a mechanism would normally lead to a phase-change of the *second* order, type B_1, p. 8. Lennard-Jones and Devonshire then introduce the further assumption that the energy gain on so transferring a molecule *depends on the lattice spacing* (they assume a power-law) as well as being a function of n. They succeed in deriving a model with the right thermodynamic behaviour, the lattice becomes unstable when n approaches $N/2$, and the process of melting is accompanied by a sudden jump in the lattice spacing, or density, as it should be. The two forms of the theory (which mainly differ by the use of the Bethe and Bragg-Williams approximations for handling the order-disorder part of the problem) are compared with experimental results on a few substances whose molecular interaction functions can be taken as fairly well known from data on the equation of state of the gases. The agreement with experiment is fair.

Two criticisms of this model can be made. First of all it is hard to reconcile the physical picture, in which approximately *half* the molecules have to leave their regular lattice sites before melting occurs, with other forms of the "hole" model of a liquid, in which the number of "holes" in a liquid near its melting point is only a small fraction of the number of molecules present. (These numbers become comparable only near the *critical* point of the liquid.) An effect that must exist, and that has not been taken into account in this model, is that the *normal modes* of the solid must change as more and more molecules enter interstitial sites, and this might result in a significant change, for example, in the Debye temperature, and lead to the occurrence of the phase change while n/N is still small. This point is being investigated by Kirkwood *et al.* (private communication). A second serious criticism is that the Lennard-Jones–Devonshire theory definitely predicts a *critical temperature for the liquid-solid transition* at a pressure that, for argon and even more so for helium, is well within the ranges of pressures that have been studied experimentally without any critical point having been found. This shows that the theory in its present form is definitely too crude.

A programme for a rather simpler theory on the same lines was put forward by Frank (1939). He also proposed to describe the appearance of vacancies in the lattice by means of a "Bragg-Williams-like" theory, but brought forward arguments to suggest that the energy needed to create a further vacancy would not be just a linear function of the number of vacancies already present, but might vary in some more complicated way, and should thus lead to a first-order transition, as required.

(b) Theories which assume different models for Solid and Liquid

As an example of a theory of this kind we select that given by Fowler

and Guggenheim (1939) in which we derive a melting curve by describing the solid and liquid by two *related*, but *not* identical models. For the liquid we use the harmonic oscillator model of Mie (1903), which is based on the idea that a typical molecule may be thought of as moving in a field that represents the effect of neighbouring molecules, this field being considered to be parabolic. Actual calculations (Lennard-Jones and Devonshire (1937)) show that this may be a good approximation at not too low densities, but that at low densities a "square-well" potential may be as good or better. As Fowler and Guggenheim point out, *Statistical Thermodynamics*, Chap. 8, it is really best to use a model of the same "degree of crudity" for solid and liquid, the appropriate solid model for comparison with the simple harmonic oscillator model of the liquid being the Einstein single frequency model.

The partition function per molecule of solid is, see Chapter IV, equation (19) (p. 73),

$$e^{\chi_s/kT}\left(\frac{kT}{2\pi m\nu_s^2}\right)^{3/2} \tag{2}$$

while that per molecule of liquid is

$$e^{(\chi_l+kT)/kT}\left(\frac{kT}{2\pi m\nu_l^2}\right)^{3/2} \tag{3}$$

the extra factor e arising from "communal entropy" (p. 70).

Equating these two partition functions leads to the melting curve as usual. The reader is referred to Fowler and Guggenheim, Chap. 8, for a comparison of this theory with experiment. As there are various unknown constants in equations (2) and (3), the experimental check is only indirect, but seems satisfactory. The difference between the form of equations (2) and (3) is a result of the "communal entropy" already referred to (p. 70). Until a more accurate theory of this is available, it is not worth attempting to refine equations (2) and (3) by quantum treatments or by postulating a frequency spectrum.

As a rather different example of this use of two distinct models, we may mention the so-called "cybotactic" theory of melting. This theory amounts to treating the liquid as statistically equivalent to an equilibrium "mixture" of solid crystallites of all sizes. This does not necessarily mean that fragments of crystal are supposed to be physically present in the liquid, but it is assumed that the partition function of the liquid can be described with sufficient accuracy as some sort of geometric mean over the partition functions of crystallites of all sizes. This assumption would be consistent with the actual physical presence of crystallites, but would be equally consistent with some very much weaker assumption, e.g. that a typical liquid molecule spent certain fractions of its time interacting strongly with 0, 1, 2, 3, . . . other molecules and only weakly with the remainder, this idea being not unlike

the Mayer (1940) picture of clusters. This sort of picture, due to Stewart and Benz (1934), suggests an alternative attack on the difficult communal entropy problem. We give a slight modification of a rough but suggestive treatment on this basis due to Mott and Gurney (1938). Plainly, the appropriate value of the communal entropy will depend on the mean number of molecules in a crystallite, which number we call n. The extra energy associated with the liquid, as compared with the solid, is proportional to the total "surface of misfit", which is, for an assembly of N molecules, proportional to the number and to the mean surface of the crystallites, that is

$$E_m \propto (N/n)n^{2/3} \tag{4}$$

We estimate the entropy associated with each crystallite as being roughly proportional to log (the number of different ways in which it can be rotated about one or more axes so as to give physically distinguishable configurations). This number is roughly proportional to the greatest perimeter of the crystallite or to $n^{1/3}$, so that the estimated communal entropy for N/n crystallites is

$$S_m \approx (N/n)\boldsymbol{k} \log (n^{1/3}) \tag{5}$$

Evidently (5) can only be expected to hold if n is fairly large, but, from the Mayer cluster theory (1940), we expect this to be the case near the freezing point, at all events as long as we are well below the critical temperature of the liquid. As we have already seen from Chapter IV, the conclusion from the Mayer theory is that large "clusters" appear simultaneously with the appearance of the liquid state, or, in more familiar language, any molecule in the liquid is likely to be found in the near neighbourhood of a large number of others. As we follow the melting curve to higher pressures, we shall eventually pass the liquid critical temperature, and we shall arrive at that portion of the melting curve for which the solid "melts to form a gas". Now it is well established experimentally that no anomaly in the melting curve can be found at the critical temperature of the liquid. As we go up the melting curve, we shall be going further from the critical region, and n, the mean size of aggregate in the fluid phase, will presumably be getting *smaller*. We can estimate that, once the mean size of crystallite has become fairly small ($n=5-10$, say) no further increase of entropy should occur as a result of breaking the crystallites up still smaller. We already know that the maximum increase of entropy that can occur due to allowing all the molecules to wander about the whole assembly, instead of each being confined to a single lattice cell as in a crystal, is $\boldsymbol{k}$ per molecule. Thus, we should expect equation (5) to hold at large values of n, and for the entropy to approach a constant value comparable with $N\boldsymbol{k}$ for n small. On the other hand, it will always be a fairly good

approximation to use (4) for all values of n. The contribution to the free energy associated with the variable n is then given roughly by

$$\begin{aligned} F(n) &= An^{-1/3} - BTn^{-1} \quad (n \text{ large}) \\ &= An^{-1/3} - NkT \quad (n \text{ small}) \end{aligned} \tag{6}$$

The expected behaviour of $F(n)$ as a function of $n^{-1/3}$ is then as shown in fig. 13, so that, at a certain temperature T_m, a state in which n is large (solid) will be in equilibrium with one in which n is smaller (liquid or gas). Thus, this simple model gives us, in principle, a physical theory of melting, but numerical estimates of the constants A and B are likely to prove difficult.

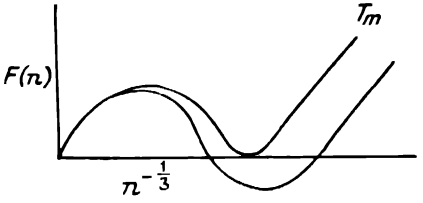

Fig. 13. Mott and Gurney's theory of melting.

5.4. Models that attempt to describe all three Phases

We have already mentioned the work of Kirkwood and Monroe (1941) which attempts to show that a theory based on the distribution fuction should predict a transition corresponding to solidification at sufficiently high densities. Their theory predicts, in contrast with that of Lennard-Jones and Devonshire, that there should be no "critical temperature of melting". It predicts crystallisation even for the rigid sphere model at sufficiently high densities. (This is to be expected geometrically, ordered close packing giving a smaller volume than random arrangements.) The integral equation of Born and Green (1946; 1947) also has solutions corresponding roughly to the solid state, but, here again, the Kirkwood approximation had to be used (p. 60).

Kirkwood and Salzburg (unpublished) have attacked the problem anew by deriving rigorous relations between the distribution functions and the cluster integrals, similar to those found by Mayer and Montroll (1941), and then have tried to show that these can be cast into forms suggesting abrupt changes in the form of the solution at the two transition points. This contention is almost certainly physically sound—it amounts to a step towards a rigorous proof of the statement that both phase-transitions can be accounted for on the basis of an intermolecular interaction function of the ordinary attractive-repulsive type.

One instance of a simple model which describes two phase transitions has been found by Temperley (1954). In an attempt to describe the behaviour of He_3 liquid he modified the equation of the "perfect Fermi gas" by introducing correcting terms of van der Waals type—a term

$-a/v^2$ being added to the free energy per atom, and the "effective volume" (determining the distribution of energy levels) being assumed less than the actual volume. This model is found to have *two* first-order transitions, one from a degenerate gas to a degenerate gas of smaller density and one from a degenerate gas to a nearly classical one. By choosing reasonable values of the van der Waals constants it is possible to obtain agreement with the melting and evaporation curves of liquid He_3 of the semi-quantitative type (some quantities reproduced well, others only in order of magnitude) characteristic of the ordinary van der Waals equation. No parameter characteristic of a lattice structure appears, so the solid phase is being treated as amorphous.

The success of this extremely crude model appears to be due to the combined effects of the Fermi-Dirac statistics obeyed by He_3 atoms and of their weak interactions. (In the not dissimilar cases of electrons in metals and of nuclear theory, it is also known that extremely crude models can give worth-while results.) Accordingly, such a model is unlikely to be applicable to other liquids.

5.5. Irreversible Effects associated with Melting

If theories such as those of Mott and Gurney (1938) or of Lennard-Jones and Devonshire (1939 a, b) prove to be reasonable first approximations, that is, if they serve at all as a pattern for theories of melting, we might expect to find superheating of solids and supercooling of liquids, the discussion running along very much the same lines as that of the liquid-vapour transition. One would assume, first that the equation of state can be prolonged into a metastable region as is done with the van der Waals equation, secondly that the surface energy necessary to create a small nucleus of the more stable phase is positive, so that such a nucleus is unlikely to appear by itself, but may have to be introduced from outside as a "seed".

One question that has to be considered is why superheating of a solid is, apparently, very much more difficult to realise experimentally than supercooling of a liquid. While many liquids have been cooled below their equilibrium freezing points and measurements of such properties as viscosity and ultrasonic absorption have been frequently made in the supercooled liquid region, experimental *evidence* on the possibility or otherwise of superheating of solids is hard to find in the literature, though many writers have claimed that it is impossible. It seems clear that it is difficult. Two explanations of this apparent discrepancy seem possible. First, it is quite likely that the "van der Waals-like" curve associated with the solid-liquid transition is markedly asymmetrical. See Frank (1939). If, for example, it had a form such as that shown in fig. 14, as is, in fact, predicted by the Lennard-Jones–Devonshire theory (1939 a, b), the rule of equal areas would apply, but

the limit of stability would be much nearer the stable two-phase region, and would correspond to a much smaller metastable range of density, and therefore of temperature, for the solid than for the liquid. A second suggestion has been made by Frenkel (1946), p. 425, namely that a uniformly heated solid really "melts" first at the surface, whereupon the remainder of the solid cannot rise above the melting temperature because a "nucleus" has already been formed by the melted surface layer. If this were so, he argues further that it should be possible by special methods, e.g. by heating electrically, by focusing of radiation by means of a lens or by high-frequency heating, to superheat a solid internally. (Frenkel states briefly that such experiments have, in fact, been carried out with positive results but gives no references.) Unfortunately, both of Frenkel's points seem to be applicable only to those few solids (e.g. ice, antimony, bismuth) which *contract* on melting. So far as is known, the surface tension of a solid is positive, i.e. tends to compress the layers near the surface of the solid, and it would thus usually tend to *raise* the melting point of such layers, not to lower it. Another possibility is that the sum of the energies required to create the two surfaces, solid-liquid and liquid-vapour, may be less than the energy required to create a single solid-vapour surface. If this were so, then a crystal with a few of its outer layers "melted" (so as to form a flat liquid nucleus) would be more stable than the dry solid, but it then becomes extremely difficult to see how a *sharp* transition could occur at all. (The liquid-vapour transition would be "smoothed out" if the surface energy were negative, i.e. if it tended to *favour* the formation of small vapour bubbles or droplets of liquid.)

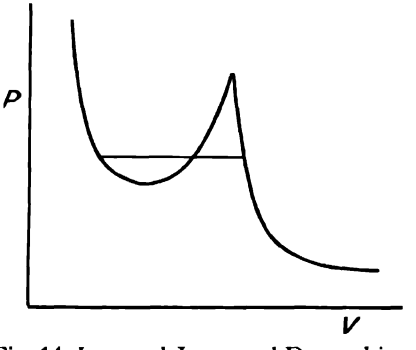

Fig. 14. Lennard-Jones and Devonshire theory of melting.

Moreover, even if it is taken as experimentally established that a solid *can* be heated internally above its melting point, this does not really *prove* that we are realising the metastable portion of a "van der Waals-like" curve. Consider what would happen if the solid expanded on melting. Local melting would set up a high pressure inside the small liquid nucleus (confined by the remainder of the crystal) and so would raise the melting point of the solid in the neighbourhood of this liquid nucleus. This would mean that a rise in temperature would be necessary in order to melt some more solid so as to expand the liquid nucleus. Thus, an experiment of the type described by Frenkel would be expected

to lead to a measurable rise in internal temperature, without bulk melting, even for a solid that, under zero stress, was incapable, for any reason, of entering the metastable region at all.

This question certainly deserves to be investigated further. It may well be that there is some inherent instability of the boundary surface of a solid such as the tendency to become "molecularly rough" as the temperature rises, Temperley (1952), but there is, at present, no explanation of why this instability should happen just at the bulk melting point. (If it happens at a lower temperature it will tend to "smear out" the transition, if at a higher temperature it is too late to be of any help.)

The converse problem of the persistence of the liquid state below the melting point has been extensively studied, as it is of great technical importance. We may divide liquids into two types, the first containing water and the metals, for which very considerable supercooling is possible under proper conditions, but for which there seems to be a quite definite low temperature limit to the liquid state (as would be expected on the basis of a "van der Waals-like" theory) and those liquids which form "glasses" under ordinary conditions and may be quite difficult to crystallise. The silicates are typical examples of glasses, and are very difficult to crystallise. As usual, the distinction is not sharp, for there is an intermediate range of substances (e.g. borates, sulphur, glycerin) which can be solidified in the glassy or the crystalline states at will. Water *has* been obtained in the glassy state, but special experimental precautions are required. Pryde and Jones (1952).

A review of the literature on the glass-like state is given by Winter (1952). The characteristic feature of a glass is that, when heated, it softens gradually and has no sharp melting point. It may undergo other transitions at temperatures well below the softening point, but these, too, are spread over finite ranges of temperature. No satisfactory explanation of this difference between the two types of liquid seems to have been given. Winter (1952) has pointed out empirically that a glassy state can be expected for a substance if the interaction energy between molecules exceeds 60 kilocalories per mole, but the principle of corresponding states suggests that the result of increasing the interaction between molecules should be simply to raise the melting point. The point that does seem to need explaining is why, in ordinary liquids, the viscosity stays quite small right up to the melting point whereas the viscosity of glasses near the softening point is enormously high, usually of the order of 10^{10}—10^{12} poise. If such an explanation can be found then, as noted on p. 33, it is to be expected that the transition to the crystalline state will be "smeared out" simply because of the very long time intervals involved. This is borne out by the fact, known to practical glassworkers, that old glassware often crystallises spontaneously when

heated slightly, which suggests a transition time of the order of months or years.

The problem is then that of explaining the high viscosity of such liquids, and it seems that this is possible on the basis of Bernal's theory of associated liquids, quoted by Fowler and Guggenheim (1939). According to this, associated liquids can be divided into three types, according to the number of possible points on each molecule that can serve as temporary points of attachment for other molecules, e.g. through the formation of hydrogen bonds. If there is one such point, as in the alcohols, association stops when double molecules are formed; if there are two, as in sulphur, the tendency is to form rings and chains; if there are more than two, as in water, very many molecules are all loosely bound to one another. (This classification is quite analogous to that of polymers, the three possibilities corresponding respectively to dimers, long-chain polymers and cross-linked polymers.) The most favourable conditions for the appearance of high viscosity is the formation of long chains (as opposed to rings or roughly spherical aggregates). (The anomalous behaviour of the viscosity of sulphur, which increases with temperature for part of the liquid range, has been accounted for on the basis that rings are being "broken open" into chains as the temperature rises.) An associated liquid consisting mainly of *closed rings* or nearly *spherical* aggregates (the latter might be expected in water) should not show abnormally high viscosity, but should behave roughly like a "simple" liquid of effective molecular weight much greater than its formula weight. This behaviour is particularly noticeable for water, whose melting and boiling points are exceptionally high for a substance of such low molecular weight. Thus, we are led to believe that glasses are more likely when the liquid has high viscosity, which will be the case when the molecules form chains, i.e. when there is an average of two effective points of attachment per molecule, and this seems very reasonable for the silicates and borates and for glycerine (three hydroxyl groups).

The behaviour of "non-glassy" liquids when supercooled has also been studied intensively. Borelius (1952) gave an ingenious derivation of the degree of supercooling to be expected. He takes the observed curve of "configurational" entropy against temperature and attempts to "reconstruct" a smooth "van der Waals-like" curve relating configurational entropy with temperature. (The "configurational" entropy is determined from the observed specific heat curve after subtracting from it the "normal" specific heat represented by a Debye function.) By using a quartic function (fig. 15) he is able to join up the two disconnected parts of the entropy curve by a smooth S-shaped curve which obeys the rule of equal areas, and then shows that the minimum of this curve agrees satisfactorily with the observed limit of supercooling

for the three metals (lead, tin and mercury) for which satisfactory data are available. This theory predicts possible superheating of the solid comparable with the supercooling of the liquid, and is thus in partial disagreement with the facts.

It has been found that the most favourable conditions for survival of metastable liquid exist when it is in the form of fairly small drops, and, as one might expect, under conditions as clean as possible. The supercooling of metals has been studied by Turnbull in a series of papers in which he gives also a survey of older work (1950). He concludes that the kinetics of solidification are satisfactorily described by a nucleation theory, Fisher, Holloman and Turnbull (1948), of the type that was applied by Fisher, see p. 90, to the problem of a liquid under tension with fair success.

The supercooling of water has also been much studied, on account of its meteorological importance. See, for example, Vonnegut (1948), Frank (1946), Cwilong (1947). It is certainly known that under moderately "clean" conditions water can be supercooled to −40°C and that water in this condition exists in some types of cloud, causing icing on aircraft. Various attempts that have been made to produce rain artificially are, in fact, nothing more than attempts to "touch off" the freezing of such supercooled water. The ice crystals then collide with more supercooled drops which also freeze, and so eventually become large enough to act as nuclei for raindrops, whereas, if not "touched off" the small drops of supercooled water might persist for a very long time, not growing appreciably by direct condensation from the vapour phase because only a very small pressure of vapour can be present at such temperatures. A survey of the literature is given by Pryde and Jones (1952). In conditions likely to occur in clouds, it seems unlikely that water can supercool much below −40°C, though this has been disputed by Rau (1946).

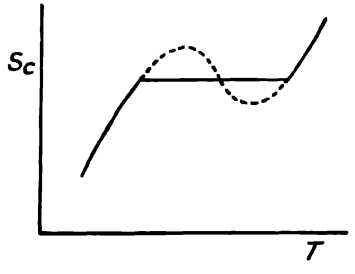

Fig. 15. Borelius theory of supercooling.

5.6. Is there a Critical Temperature for Solids?

This question has led to a great deal of discussion, and must still be considered to be completely open. There are at least three possibilities, but before enumerating them, we make one remark. At pressures that can be applied in the laboratory the outer electronic shells of atoms in a solid are barely in contact with one another. It is almost certain that, if sufficient pressure could be applied to any substance, a fundamental

change in these outer orbits would occur, sufficient to give us, in effect, a chemically different substance. (For example, some geophysicists consider that, at sufficiently high pressures, hydrogen would make a transition to a metallic state.) At still higher pressures and temperatures matter would become an assembly of free electrons and partially stripped nuclei. Naturally, we are excluding all effects of this kind from consideration. On this understanding we can put forward three alternative hypotheses.

(a) The melting curve terminates abruptly, like the vapour pressure curve, and all difference between the solid and fluid phases disappears above this point.

(b) The melting curve "fades out" gradually, i.e. as we follow it to higher and higher temperatures, the properties of the two phases become more and more alike without their ever becoming identical.

(c) A well-marked difference between the two phases persists throughout the whole length of the melting curve, unless and until this is brought to an end by some other transition of the types mentioned above.

Münster (1950; 1952) has attempted to prove that the melting curve must always end at a critical or triple point, but his argument depends on the assumption, which is by no means obvious, that, at regions high up on the melting curve, the degrees of freedom of the assembly behave classically from the point of view of statistical mechanics. Bridgman (1934; 1949) argues strongly that the trend of his curves are not what one would expect if they were to terminate in a critical point, and Simon (1952) shows that, for the case of helium, the entropy of melting is actually increasing as we travel up the curve in the direction of increasing temperature, at least as high as 25°K (compared with a liquid-vapour critical temperature of 5·2°K). Such behaviour would certainly not be expected if we were approaching a critical point, and it also seems to be evidence against behaviour of type (b) above for which the entropy of melting should vanish. The question whether helium can be considered a "typical" substance, in the sense that the melting curves of other substances should be predictable from that of helium by some application of the principle of corresponding states, is a difficult one. Semi-empirically a "scaling" of the fusion curves is possible, Simon (1952), but the relative importance of "quantum" effects, such as zero point energy, will be very much greater for helium than it is for other substances at corresponding points on the curves, and there is no definite reason why the importance of quantum effects should diminish as we travel up the melting curve.

We may sum up the present position by saying that present evidence is consistent with melting curves being of types (b) or (c) above, which is the prediction of Kirkwood and Monroe (1941). Such experimental

evidence as is available seems to show that the entropy of melting increases as we travel along the melting curves towards *higher* pressures and temperatures, which is evidence against hypothesis (b).

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Note. "Paris Conference" refers to the Paris Conference on Phase-Changes.

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CHAPTER VI

Solutions

Order-Disorder in Alloys, Adsorption and Related Problems

6.1. Methods for a preliminary Study of these Problems

We now consider some mathematical treatments, that can be applied, *mutatis mutandis*, to discussing a wide variety of physical problems. To pass from the equilibrium theory of one of these problems to that of another we, in general, have only to make appropriate transcriptions of the thermodynamic variables, but the nature of these transcriptions is not always obvious. This arises because we always study any type of assembly subject to certain *constraints*, these being chosen so as to fix the equilibrium state uniquely. If we pass from one type of assembly to another, the changes to be made in the extensive variables are usually obvious from physical considerations, but those for the intensive ones may have to be determined by comparison of the appropriate thermodynamic or statistical formulae. When these two stages of the transcription are completed, it may turn out that we are trying to set out the new problem in an unfamiliar form, or under constraints that cannot, in practice, be applied. It is then necessary to make an appropriate transformation of the *thermodynamic potential*. A transformation that very often occurs here corresponds to the passage from the "ordinary" to the "grand" partition function in statistical mechanics, the corresponding thermodynamic transformation being from an assembly that is specified to contain definite *numbers of molecules* to one in which we fix the corresponding *partial potentials*. This fact, that the thermodynamic transformations seem complicated (though they become less so when considered in the three stages outlined above), has meant, in practice, that the basic similarities between a large number of different types of phase transition were only realised gradually. For example, the close *formal* relationship between the problem of the evaporation of a liquid and the ferromagnetic problem was first explicitly pointed out by Yang and Lee (1952), whereas the relationship between the theory of ferromagnetism and corresponding theories of order-disorder in alloys, adsorption, freezing, and of the so-called λ-phenomenon in solids had been already pointed out by a number of workers. We emphasise that this remark only applies to the basic similarities between many theories of the equilibrium state, the non-equilibrium and irreversible effects still having to be considered

separately for each type of transition. (Separate consideration is also made necessary by the fact that alternative theories do exist for some of these phenomena, e.g. solubilities, freezing, evaporation, ferromagnetism, for which the process of transcription we are now discussing may not be appropriate.)

We shall first illustrate the process of transcription by some examples, and shall then develop some of the forms that the theory can take when applied to these various phenomena. The actual types of interaction that can be dealt with, with any approach to rigour, are highly idealised. We shall be referring constantly to two models—the first, applied by Weiss (1907) to ferromagnetics, and by Gorsky (1928), Bragg and Williams (1934) and others to alloys and solutions is equivalent to the assumption that interactions may be treated as if they had an extremely long range, so that, for example, in a magnetic material the interaction of two atoms a long distance away has just as much influence on the total magnetisation as has the interaction of two neighbours. Such a model will be referred to as a "Weiss-type" model. Another assumption that has been much used is that the only interactions influencing the magnetisation are those between nearest neighbours, all other interactions being neglected. We shall refer to such models as "Ising type" (1925).

6.2. Comparison of these approximate Approaches

With a Weiss-type model, the rigorous statistical mechanical consequences can usually be deduced quite easily, but an interaction of this kind never occurs in nature. If it did, its consequences would be the same whatever the type of crystal lattice involved. The Ising-type model should give a very good approximation in certain types of problem, e.g. in ferromagnetism where the relevant interaction, the "quantum mechanical exchange" effect, probably falls off extremely rapidly with distance, or in the theory of solutions, where one will be concerned with inverse sixth-power interaction energies of van der Waals type, or in the theory of alloys, where it is unlikely that any noticeable effect of a "misplaced" atom can extend beyond a few lattice distances. Unfortunately the derivation of the *exact* consequences of the Ising-type approximation has proved an extremely stubborn mathematical problem. A review article, describing the mathematical methods that have been successfully tried, and the results obtained to date, has been published by Newell and Montroll (1953), to which the reader is referred for detailed accounts of the methods. These range from matrix theory to the theory of graphs. So far, only certain two-dimensional lattices have yielded any *exact* results, and these all belong to the class of lattices which possess "topological duals". We shall return to such lattices later on (p. 160).

Preceding and overlapping these investigations have been others, aimed originally at solving the Ising problem by successive approximation methods. A review of the earlier work, including detailed comparisons with the then available experimental material, was given by Nix and Shockley (1938), the emphasis then being on the applications to order-disorder phenomena in alloys. Many more investigators have since taken up these problems, new methods have been devised and applied to more complex models and problems, for which there is at present no hope of an exact treatment. For reviews of progress on these lines see Guggenheim, *Mixtures* (1952), and Rushbrooke (1952). Some of the approximate methods used have turned out to be equivalent to one another, and accordingly the same formal results can be, and are, expressed in a wide variety of different ways, quite apart from the fact we have already mentioned, namely that the same results can be applied in a number of different physical contexts.

Yet a third line of attack on the "problem of the Ising model" has been the devising of workable methods for obtaining *series expansions* of the partition function, it being hoped that ways could be found of bridging the gap between temperatures that are "low" and "high" compared with the Curie temperature. Again, these methods can be applied to fairly complicated three-dimensional lattices, for which no *exact* results are likely to be found for some time. The convergence of such series always turns out to be disappointingly slow when we approach the Curie temperature, while the labour required to compute more terms increases rapidly. It is sometimes possible to make a fairly reliable estimate of the position of the Curie temperature, and of the probable behaviour of the partition function in its neighbourhood, but it sometimes happens, particularly for the three-dimensional lattices, that the magnitudes and signs of the known terms are so irregular that no plausible law of formation can be guessed. (Sometimes this situation is improved if an expansion with respect to some slightly different function of the temperature and interaction energy is used.)

Broadly speaking, the situation facing workers using these second and third lines of approach is the same rather depressing one, and a comparison of the approximate methods with the series expansions only serves to deepen the gloom. It was at first thought that the fact that two successive approximations seemed to be agreeing well with one another was a sign that they were both close to the *correct* consequences of the model, but a comparison with the known terms of the series solutions has revealed that this is hardly ever the case, and that the convergence, for example, of Bethe's (1935) first, second, third . . . approximations to the exact partition function would be very slow. For a discussion of this point, see Barker (1953), also Guggenheim, *Mixtures* (1952). Some exceptions to these rather sweeping

statements must perhaps be made in favour of some approximations introduced recently by Kikuchi (1951) and Cowley (1950). Comparison with other treatments in two dimensions shows that Kikuchi's approximation, which is mathematically quite simple (though its derivation is complicated), is equivalent to the best previously known approximation, obtained by a much more elaborate method, Kramers and Wannier (1941), while Cowley's treatment (1950) gives a better account than most of the other approximate methods of the qualitative behaviour of the partition function in the immediate neighbourhood of the Curie point. A numerical comparison of some of the known approximate methods will be given later (p. 155).

6.3. Comparisons with Experiment

The attempts to compare the consequences of the Ising-type model with experiment has led to a situation that does not seem to be paralleled anywhere else in physics. We have already seen that the interactions that it attempts to represent cannot be described with any degree of reality by means of a Weiss-type model, and other cogent arguments (for example, that a Weiss-type model is, strictly speaking (see p. 208), incompatible with the existence of domains in a ferromagnetic) will be given in this and the next chapter (pp. 119, 201), showing clearly that a theory with such a basis is altogether too crude to give more than a semi-quantitative account of the facts (of the kind achieved by the van der Waals theory). On the other hand, we shall meet instances (pp. 209-15) which show clearly that the nearest-neighbour assumption is also insufficient to describe many of the facts. In ferromagnetism, some of the arguments of Néel (1934) are particularly cogent in this respect, while some of the experimental facts about antiferromagnetism clearly require interactions that extend beyond nearest neighbours (p. 221). In the ferromagnetic case, Tredgold (1953) has recently shown that attempts to improve the Ising model, by replacing its averages over spin directions by something more in keeping with what is called for by the quantum theory of exchange interactions, are *not* likely to lead to any better agreement with experiment. This again suggests that interactions of longer range than just between nearest neighbours have to be considered explicitly. Let all these points be conceded; the fact remains that the nearest-neighbour model cannot yet be compared with experiment in the way that is customary with physical theories. So many attempts have been made to do so, and so much confusion has emerged, that it seems worth while to set out the following summary of the logical position.

In developing a physical theory we:

(a) Choose the model.

(b) Attempt to derive its quantitative consequences.

(c) Try to estimate the effects of any approximations we have had to make during step (b).

(d) Compare the results of (b), as modified by (c), with experiment.

(e) Try to estimate the effects of generalising the model to include any extra effects known to be present.

(f) See whether such attempts tend to improve or worsen the agreement between theory and experiment.

(a) Calls for several comments. We chose the Ising model for two reasons, first because it is a reasonable first approximation to an interaction of any type that falls off rapidly with distance (though various writers have pointed out that it is not a good representation of the actual quantum mechanical consequences of exchange interaction (p. 183)), secondly because it seems hopeless to try to estimate the probable consequences of more complicated assumptions until we know the correct consequences of this one with reasonable certainty.

(b) We have already noted the difficulty which arises because most of the successive approximation methods tried show very poor convergence when compared with known exact results. Consequently, it is difficult to achieve anything on the lines of (c), or to set *limits* on the errors likely to be introduced by the approximations. The results actually required are various differential coefficients of the partition function rather than the partition function itself. This magnifies the errors caused by the approximations.

(d) The agreement between the consequences of most of the approximate methods with experiment is often very poor, even after making allowance for the fact that difficulties in obtaining reliable data near a transition point often occur; reasons for *expecting* such difficulties have already been given (p. 49). As typical examples of such comparisons, reference should be made to the "calculated" and "observed" specific heat anomalies in Nix and Shockley's review (1938). The "calculated" anomalies are almost always too "low" and too "fat". There is a decided tendency to bring this fact forward as *evidence, by itself, of the inadequacy of the nearest-neighbour model*, but comparison of the consequences of the approximations in two dimensions with the known exact results now available for some two-dimensional lattices leaves little room for doubt that replacing the approximations by a proper three-dimensional calculation would, in nearly all cases, lead to a considerable improvement in agreement between theory and experiment. (See also Domb (1952).) In the language of Chapter II, the observed anomalies can, in practically all cases, be more satisfactorily interpreted as "infinities" in the specific heat (Type C in our classification) rather than as "jumps" in the specific heat (Type B in our classification). In some cases, e.g. the α-β quartz transition, β-brass,

Moser (1936), it has been shown that the observed specific heat anomalies can be well represented by $\Delta C \propto |T_c - T|^{-1/2}$, which is extremely suggestive when compared with the exact two-dimensional result, $\Delta C \propto \log |T_c - T|$, Onsager (1944; 1947).

(e) We often know perfectly well the type of correction that can and should be made, for example the consequences of thermal expansion of the crystal lattice, Eisenschitz (1938), or the effect of the transition on such parameters as the Debye Θ describing the lattice vibrations or on the Brillouin zone structure describing the conduction electrons of a metal, Mott (1937). In some cases, consideration of such "side-effects" is vital to the theory, for example the Lennard-Jones and Devonshire theory of melting (1939) would not even be qualitatively right unless explicit account were taken of the change of interaction energy with density. As noted above (p. 102), there is reason to believe that the above theory could be further improved if the effect of the lattice vibrations were considered explicitly. In another set of cases, e.g. the magnetic one, the "side-effects", anisotropy and magneto-striction, have to be assumed separately, as they are vital to a proper understanding of domain effects. One would like to see a theory predict these "side-effects" as natural consequences, but this the Ising-type model palpably fails to do. In a third set of cases, e.g. order-disorder phenomena, it is known, Eisenschitz (1938), that taking into account possible relationships between density and thermal expansion and the ordering energy could, in principle, lead to a considerable improvement in the agreement of "calculated" and "observed" specific heat anomalies, but we are faced with the usual difficulty that this form of correction involves extra adjustable constants. It is at present very hard to see how the influence of these "side-effects", which certainly must occur, can be separated from the improvement in the agreement with experiment that will, as we have just seen, also certainly occur when the consequences of the simple nearest-neighbour model in three dimensions are more exactly known. The situation is even worse than the one that usually arise with "adjustable constants", for which it usually proves all too easy to find values that "fit" the data. Here we have, at present, no means of knowing (except in order of magnitude), the amounts, or even the signs, of the discrepancies that are to be removed! As we have just seen, there is every prospect that the present big discrepancies between "theory" and "experiment" will be *reduced* by better theoretical treatments and some may even be reversed in sign. Item (f) cannot, then, be carried out at present. At present, then, we are not really in a position to "decide between" the "Ising" and "Weiss" types of model by "comparing them with experiment and seeing which gives a better representation of the facts." Attempts that are frequently made to use the Weiss theory, e.g. to "decide" the effective number of

electrons per atom that are contributing to ferromagnetism, seem to be altogether premature in the present state of knowledge. It is perfectly true that, e.g. with nickel, the assumption $S=\frac{1}{2}$ gives decidedly better agreement with the measured spontaneous magnetisation as a function of temperature than does $S=1$. See fig. 29 (p. 201). Before drawing any conclusions from this fact, it is advisable to reflect that the shape of the spontaneous magnetisation curve may be affected considerably by the "effective range" of the interaction. The form of this curve is known for a few examples of the Ising model, Yang (1952), Wakefield (1951 a, b), Potts (1952), see figs. 30 and 31 (p. 202) (unfortunately only for cases corresponding to $S=\frac{1}{2}$), for which it is entirely different from the Weiss model, descending much more sharply than the latter in the region of the Curie point. As a further complication, a Stoner-type theory (p. 192) (in which the electrons responsible for ferromagnetism are free to move about the lattice, although we still assume a "long-range" type of interaction) can also give a spontaneous magnetisation curve quite different from the Weiss model. See fig. 27 (p. 194). One slight clue does seem to show that *neither* type of theory, Weiss or Ising, is a particularly good approximation for a ferromagnetic. It is well known that, if we plot a "Curie line" (inverse of susceptibility against temperature) we get, experimentally, a quite noticeable curvature of the line just above the Curie point. According to any theory of Weiss type this line should be accurately straight, whereas according to an Ising-type model, Domb and Brooks (1949; 1951), the curvature should be very marked, and should extend over a considerable temperature range, the departure from the straight line being greater than is ever observed. Néel (1934) has attempted to estimate from the actual curvatures found in practice the "effective number of neighbours", and puts it at something like 750, which would mean that the "effective interaction distance" would be of the order of 10 lattice distances. It is certainly hard to believe that *exchange* effects could extend as far as this, but it certainly seems as if the Ising model may be an over-simplification of the magnetic problem. According to a theory of Stoner type (1938), in which we suppose the electrons free to wander all over the crystal, instead of being bound near a single lattice point, slight curvature of the "Curie line" is predicted. Here again, we have a choice between possible explanations—the curvature may be a measure of the "effective range of the interactions", or of the "tightness of binding" of an electron to a lattice point, and no means of "deciding" between these explanations seems in sight at present.

It has seemed necessary to anticipate some of the results that belong more properly to the following chapter in order to illustrate this discussion. The problem of exactly *how* we "assess" a "theory" of a phase-transition is partly a philosophical one, some of the accepted

criteria of a "good" or "bad" scientific theory breaking down completely, and this situation seems at its acutest in the fields we consider in this and the following chapter. The disagreement of (theory plus approximations in working it out plus corrections for "side effects") with experiment is, as always, a danger-signal, though it does *not* follow that we are in a position to find out the cause of the trouble as there may be quite a number of plausible explanations. On the other hand, the emergence of a theoretical curve passing through the experimental points is not *quite* the occasion for rejoicing that it is in other branches of physics, and extreme cases may arise, such as the variation of the spontaneous magnetisation with temperature that we have been discussing, where it is of almost no significance at all.

The comparisons with experiment that follow in this and the following chapter must be considered in the light of this discussion. One wishes to avoid casualness, but an elaborate comparison of "calculated" and "observed" results would, in most instances, be completely out of place. The situation revealed in Chapter IV is not dissimilar. The conclusion we reached there, on physical grounds, was that the "Mayer" and "distribution-function" types of theory were more likely than are the older models to lead to fresh advances in our understanding of liquids and of their changes of state, but it would be almost impossible to produce any *numerical* evidence in support of such a contention at the present time. (The present position, as a matter of fact, is that the consequences of some of the older liquid models can be worked out completely and compared with experiment, which cannot yet be done for the newer ones.)

In both fields, then, the older models are valuable because they assist in physical insight, and can be used, pending the development of something better, provided that reasonable attention is paid to determining the probable "range of validity" of each one. As with the van der Waals theory, this range *may* be wider than one expects, because of such factors as the mutual cancellation of correcting terms.

6.4. The Transcription of a Mathematical Model into different Physical Contexts

We give a simple case, applied to a number of different problems, by way of illustration. This subject has been discussed at length by a number of writers, e.g. Fowler and Guggenheim (1939), Rushbrooke (1949), Brooks and Domb (1951), Yang and Lee (1952), while the first explicit use of transcriptions seems to have been due to Fowler (1936) and Peierls (1936 a). We have already indicated that, in general, all three types of thermodynamic variable, intensive, extensive and thermodynamic potential, may have to be changed, and accepted usage may also call for a change in the zero of energy. The simplest possible

model has been taken in order to *illustrate* the principles involved, but it might be a difficult matter to *state* these principles in a logically unassailable form, because of the very great variety of cases that have occurred.

6.4.1. The simple Weiss Model

We consider the Weiss model of a ferromagnetic in its very simplest form in which each atomic magnet is allowed only two possible orientations with respect to the applied field H, of energies $\pm\mu H$. To take account of the effect of interactions; we suppose that the assembly contains a total of N atoms, of which n are "positively" oriented while $N-n$ are oriented in the "negative" direction. The number of ways in which n positive atoms can be selected out of a total of N is $\binom{N}{n}$, and, if we write $M=(2n-N)\mu$, for the total magnetic moment of the assembly, the Weiss model is equivalent to assuming the Boltzmann factor for the whole assembly to be exp $\{(MH+\frac{1}{2}\nu M^2)/\boldsymbol{k}T\}$, so that the partition function for the whole assembly is

$$f=\sum_{n=0}^{N}\binom{N}{n}\exp\left[\{(2n-N)\mu H+\tfrac{1}{2}\nu\mu^2(2n-N)^2\}/\boldsymbol{k}T\right] \qquad (1)$$

where ν is a constant. The most probable value of n can be determined by a number of equivalent methods, for example one can pick out the maximum term in (1) by differentiation with respect to n, using Stirling's formula for the factorials, and we find that

$$2\bar{n}-N=N\tanh\left[\{\mu H+(2\bar{n}-N)\nu\mu^2\}/\boldsymbol{k}T\right] \qquad (2)$$

giving us an implicit equation for $2\bar{n}-N$. The "magnetic Gibbs function" for the whole assembly, G', is given by $-\boldsymbol{k}T\log f$, so that

$$G'=-\boldsymbol{k}T\log\binom{N}{n}-\overline{M}H-\tfrac{1}{2}\nu\overline{M^2} \qquad (3)$$

and F, the Helmholtz free energy, is obtained simply by adding the term $H\overline{M}$ to G'. The following equations are then easily seen to be equivalent to (2), and any one of them can be used to determine the equilibrium value, $\overline{M}$, of M, given H and T:

$$(\partial G'/\partial M)_{H,T}=0 \quad \text{or} \quad (\partial F/\partial M)_T=H \quad \text{or} \quad \overline{M}=-(\partial G'/\partial H)_T \qquad (4)$$

It is also well known that, for $H=0$, (2) has always the solution $\overline{M}=0$ or $\bar{n}=\frac{1}{2}N$, but, for $\boldsymbol{k}T<\boldsymbol{k}T_c=N\mu^2\nu$, there are also possible non-zero values of M, which, when they exist, lead to smaller values of G' than does the zero root. By differentiating equation (2) with respect to T,

and then putting $H=0$, we can verify that $(\partial\overline{M}/\partial T)_{H=0}$ differs from zero whenever $T<T_c$, and, by expanding the hyperbolic tangent in (2), we can deduce further that

$$\lim_{T\to T_c-0}\left(\frac{\partial\overline{M^2}}{\partial T}\right)_{H=0}=\frac{3N^2\mu^2}{T_c}$$

which results in the well-known jump in the specific heat at $T=T_c$. Differentiating equation (2) with respect to H, then putting $H=0$, we find, for $T>T_c$

$$\left(\frac{\partial\overline{M}}{\partial H}\right)_{H=0}=\frac{N\mu^2\nu}{k(T-T_c)} \tag{5}$$

These results are all well known, but it has seemed advisable to show that they can be derived in a consistent way from expression (1), because the view is sometimes expressed that this model is "not internally self-consistent", and it is important to settle this point before trying to apply the same model to other phenomena.

An alternative formulation of this model is as follows: From (3), we deduce for the "magnetic Gibbs function per atom" the result

$$g'=(\partial G'/\partial N)_{\bar{n},H,T}=-kT\log\left[2\cosh\left\{(\mu H+\mu\nu M)/kT\right\}\right] \tag{6}$$

using (1) and (2) or (4), which is equivalent to what we should deduce if we thought of another atom being added to the assembly and suppose that it is exposed to an "effective field" $H+\nu M$, instead of to the field H that describes the situation in the absence of interactions. On this basis, the addition of an extra atom would contribute a factor

$$f^*=2\cosh\left\{\mu(H+\nu M)/kT\right\} \tag{7}$$

to the partition function, and if we treated this extra factor as the "partition function per atom", we could deduce all the standard results by writing $g'=-kT\log f^*$, whereupon differentiations with respect to H and T reproduce all the standard results such as (5). It is not at once obvious why these two treatments give the same results, as they appear to be inconsistent, for example we might expect f in expression (1) to be the Nth power of f^*.

It must, however, be remembered that M varies both with N and with $\bar{n}$, that is, with T, and, if we want to think of our assembly as being built up, atom by atom, we must be prepared to admit that, if interactions are present, the energy of either of the two levels into which each atom can go depends on the number of atoms that is already in that level, that is, *it depends on the temperature* apart from its dependence on the applied field H. The reason for apparent inconsistencies in this sort of situation was pointed out by Rushbrooke (1941). He shows that, if we

attempt to treat a complicated assembly with interactions by supposing, as we may do quite legitimately, that "the energy-levels depend on the temperature", we must use a generalised form of Boltzmann factor in order to preserve consistency between thermodynamics and statistical mechanics. The generalisation amounts simply to replacing the Boltzmann factor, $\exp(-\epsilon_p/kT)$ (where ϵ_p is the energy associated with adding another atom to the pth level) by $\exp(-\phi_p/kT)$, where ϕ_p is related to ϵ_p in the same way that free energy is related to internal energy in thermodynamics, that is

$$\phi_p - T\frac{\partial \phi_p}{\partial T} = \epsilon_p$$

which enables ϕ_p to be calculated if the variation of ϵ_p with temperature is explicitly known. In the present case the "energy-level" involves M, the variation of which with temperature is not available until the calculation is finished, but the mutal consistency of the two treatments is assured none the less by showing that (6) can be deduced from (3) as well as from (7).

We shall not enter into the controversial question of the correct thermodynamical treatment of magnetic bodies (for example, whether B or M is the more appropriate extensive variable. We shall actually use M because its connection with the variables used in other problems is more obvious and immediate). In the present simple model, in which we ignore magnetostriction effects, it appears that changes in the magnetic variables used imply, at most, physically irrelevant changes in the energy zero. All that we are concerned with here is that these results describe, to a satisfactory first approximation, the behaviour of some ferromagnetic metals and paramagnetic salts, the crude assumption that interactions are independent of distance being comparable with the assumptions on which the van der Waals equation is based. We defer, till the next chapter, a discussion of improved theories of ferromagnetics, and proceed to discuss the various transcriptions of this crude model to make it suitable for application to other physical problems.

6.4.2. The Antiferromagnetic Case

We first examine the effect of reversing the sign of ν. At first sight, it seems that we simply destroy altogether the discontinuous transition associated with our model, so that it is, apparently, no longer of interest in connection with changes of state. It is certainly true that, for $H=0$, the state of lowest energy *and* largest entropy is that for which $M=0$, but, if it were possible to apply a sufficiently large field, one would expect a discontinuous jump of M from zero to a finite value. Before pursuing this idea, let us consider the state of lowest energy in zero

field a little more closely. It evidently consists of *equal* numbers of positively and negatively oriented magnets. At absolute zero, some kind of spatially ordered pattern is to be expected. If the interactions were strongest between nearest neighbours and then gradually decreased with distance, it is to be expected that the atoms would distribute themselves on two sublattices in such a way that as many pairs of *neighbours* as possible were *unlike*. If the interactions were between magnetic or electric dipoles, the state of lowest energy is probably one in which alternate *strings* of dipoles are oppositely oriented. If we had one lattice-cell dimension much smaller than the other two, the oppositely oriented atoms might well sort themselves into alternate *layers* in planes perpendicular to the small lattice distance. In all these cases, the state of lowest energy, and the corresponding division into sublattices, may be supposed to be fixed by the physics of the problem, the formal results of a Weiss-type theory being the same in all such cases. We now attempt to take account of the interactions by an assumption of the same degree of crudity as that we used for the Weiss model with ν positive. We may define M_1 and M_2 as the "magnetic moments" associated with the two separate sublattices, i.e. M_1 is proportional to the difference of the number of "positive" and "negative" atoms on sublattice 1 alone, and M_2 is defined similarly for sublattice 2. The simplest assumption that we can make for the energy is that it is given by the following expression (where we do not necessarily assume that the numbers of "places" on the two sublattices are equal):

$$E=-H(M_1+M_2)-\tfrac{1}{2}\nu_{1,1}M_1^2-\tfrac{1}{2}\nu_{2,2}M_2^2-\nu_{1,2}M_1M_2 \qquad (8)$$

where $M_1=(2n_1-N_1)$=number of "places" on sublattice 1, $n_1=$ number of positively oriented atoms on sublattice 1, with analogous definitions for sublattice 2. Assumption (8) is equivalent to assuming that each sublattice is exposed to an "effective field" which contains correcting terms depending both on M_1 and M_2, according to a linear law. An assumption of this kind again means that the falling off of interactions with distance is completely ignored. The entropy associated with given values of n_1, n_2 is simply

$$S=k\log\left\{\binom{N_1}{n_1}\binom{N_2}{n_2}\right\} \qquad (9)$$

because the number of ways in which n_1 positive atoms can be selected from N_1 atoms is just $\binom{N_1}{n_1}$. Various particular cases of equations (8) and (9) have been studied by various authors, e.g. Néel (1932; 1936), Bitter (1937), Sauer and Temperley (1940), applications by the two former authors being to antiferromagnetism in crystals, and by Sauer and

Temperley to paramagnetic salts. Néel (1948) has made the further generalisation that N_1 and N_2 need not be equal, showing that this gives a good representation of the behaviour of certain magnetic compounds, which may have a net magnetic moment at absolute zero, even though the atoms on the two sublattices are oppositely oriented. Néel calls this situation *ferrimagnetism*.

This model using two sublattices has the advantage that its consequences can be easily and rapidly worked out—it being only necessary to write down the general term in the partition function with the aid of (8) and (9), the condition that this term should be a maximum then giving us two equations for the most probable values of n_1, n_2 as functions of H and T. (In general, these equations have to be solved numerically.) If $\nu_{1,2}=0$, the sublattices become completely independent, if $\nu_{1,1}=\nu_{2,2}=\nu_{1,2}$ then it is clear that we recover the original Weiss model. The present model is still extremely crude, because, although we can distinguish between the interactions of four different types of atom (+ or − oriented atoms in sublattices 1 and 2), we still rate the interaction of the very distant atoms as being as important as that of two very near one another, distinguishing *only* between atoms that lie on *different* sublattices.

For a discussion of the consequences of the assumption that some or all of the ν's are negative, the reader is referred to a review article by Smart (1953). The simplest possible case occurs when $\nu_{1,1}=\nu_{2,2}=0$, $\nu_{1,2}$ negative which is a crude representation of an interaction tending to orient nearest neighbours in opposite directions. We can build up a partition function from (8) and (9) analogous to (1) and then seek for the values of n_1 and n_2 corresponding to the maximum term, finding that, for $H=0$, the most probable values of M_1, M_2 are the roots of

$$M_1=\mu N_1 \tanh(\mu\nu_{1,2}M_2/\boldsymbol{k}T), \quad M_2=\mu N_2 \tanh(\mu\nu_{1,2}M_1/\boldsymbol{k}T) \quad (10)$$

which has solutions whether $\nu_{1,2}$ is positive or negative, the Curie temperature at which non-zero roots appear being given by

$$(\boldsymbol{k}T_c)^2=N_1N_2\mu^4\nu_{1,2}^2$$

and, if $\nu_{1,2}$ is negative, M_1 and M_2 have opposite signs, corresponding to the appearance of an antiferromagnetic ordered state, which has no total magnetisation unless $N_1\neq N_2$. One can verify that this model also shows a jump in the specific heat, and that the magnetic susceptibility has a maximum with a cusp at the "antiferromagnetic Curie point" (sometimes called the Néel point). A further feature is that the magnetic susceptibility is anisotropic below this temperature, and an elementary calculation of its values parallel and perpendicular to the direction along which the magnets point has been made by Van Vleck (1941).

6.5. The Immobile Adsorption Problem

The transcription of these models to suit the problem of immobile adsorption is almost immediate, as was pointed out by Peierls (1936 a). By an *immobile* adsorbed film we mean one in which the atoms or molecules are extremely likely to be found on certain preferred sites on the exposed surface, and that migration from one site to another is comparatively rare. We do, however, recognise the possibility that these adsorbed atoms or molecules may interact with one another, and we examine the consequences of a crude approximation such as (8). The energy of the adsorbed film is made up of two parts, the adsorption energy in the absence of any interactions, which is simply $-n\chi_0$, where χ_0 is the adsorption energy per site in the absence of interactions, while we represent the interaction by means of a quadratic term in n equal to $-\frac{1}{2}\chi_1 n^2$. (There is not usually any sense in distinguishing between two different sublattices in the adsorption problem.) The form of the interaction energy that we are assuming is slightly different from that assumed in the magnetic problem, the difference being due to the fact that *negatively oriented magnets* take part in the interactions, but in the adsorption problem *empty sites* do not interact. This difference can be allowed for during the transcription process, as we shall see in a moment. The difference between a term involving M^2 and the corresponding one involving n^2 amounts to a constant plus a linear term in n, which can both be allowed for by a proper choice of the variable corresponding to H, plus a shift of the zero of energy. (See p. 129.)

We need one further step before we can complete the solution of the adsorption problem. In practice, we study the variation of "coverage", that is, the fraction n/N of the total sites actually occupied, with the *pressure* of a gas or a vapour in equilibrium with the film at any given temperature. The condition of equilibrium is to be obtained by equating partial potentials of gas phase and adsorbed phase.

If we may treat the gas phase as nearly perfect, which is usually a good approximation unless we are the immediate neighbourhood of the *gas-liquid* critical region (*not* the region at which "critical adsorption" occurs), we should have

$$g_{\text{gas}} = kT \log\left(\frac{P}{kT}\right) - \frac{3}{2}kT\left\{\log\left(\frac{2\pi mkT}{h^2}\right) + \alpha(T)\right\} \qquad (11)$$

where the first term in curly brackets represents the result for molecules without, for example, rotational or vibrational degrees of freedom, while $\alpha(T)$ represents the correction for these. For a proof of (11) and a discussion of the possible forms of $\alpha(T)$ the reader is referred to any standard treatise on statistical mechanics. The partial potential for the adsorbed phase is, however, *not* the mathematical transcription of the

"magnetic Gibbs function per atom", for which we derived expression (6). Here we meet, for the first time, a situation in which, in the process of transcription, we have to make a change in the thermodynamic potential function. The difference arises because, in the magnetic problem, we are discussing an assembly consisting of

n positively oriented atoms out of a total of N *atoms*

whereas, in the adsorption problem, our assembly consists of

n adsorbed atoms on a total of N *sites*

so that the partition function for N *atoms* in the magnetic problem will, when transcribed, become the partition function for N *sites* in the adsorption problem. What we actually want to equate to expression (11) is the change in the Gibbs function when another adsorbed *atom* is added to the assembly. (The analogue of expression (6) would be the change in the Gibbs function resulting from adding another *site*, which is of only indirect interest in our present problem.)

We can see best what function we *do* want after making a comparison of the three main methods of statistical mechanics:

Micro-canonical ensemble : Energy and number of systems in assembly both fixed.

Canonical ensemble: Number of systems fixed but assembly allowed to exchange energy with a "thermostat".

Grand canonical ensemble : Assembly allowed to draw on the energy of, and to transfer elementary systems to or from, a much larger assembly whose thermodynamic state fixes that of the assembly, as it is acting both as a "thermostat" and a "reservoir".

For the connections between the second and third techniques and the "ordinary" and "grand" partition functions of statistical mechanics the reader is referred to Rushbrooke's book (1949), but it can be seen that an expression such as (1) can be interpreted in one of two ways (N being kept fixed in either interpretation):

(a) As the "ordinary" partition function for N systems, n of which are in the "positive" state.

(b) As the "grand" partition function for N *sites*, each of which may be empty, or may contain one system. (We may, if we like, make the convention that the energy is always $+\infty$ for $n>N$, and extend the summation over n to infinity.)

Again, we know, from general theory, that the relation between the ordinary and grand partition functions is, see Rushbrooke (1949),

$$\sum_n \lambda^n \text{ (ordinary partition function for } n \text{ atoms)} = \text{(grand partition function)} \quad (12)$$

and, further, that it is almost always sufficiently accurate to represent the left-hand side of (12) by its maximum term in the sum (at least as long as we are concerned only with logarithms of the partition functions, which is almost always the case in physical applications). It is also shown, by general theory, that, if λ^n is chosen in such a way that the nth term on the left-hand side of (12) is the maximum one, this calls for λ to be equal to $\exp(g/kT)$ where g is the partial potential per system, when n systems are present. It is open to us to regard this condition as determining λ in terms of n or n in terms of λ, whichever is the most convenient. Formally, g would be defined for an adsorbed phase as

$$g_{\text{ads}}=\epsilon-Ts+\Pi a \tag{13}$$

where ϵ and s are the energy and entropy per adsorbed atom, a is A/n, A being the total area of film and Π is the two-dimensional "boundary pressure", that is, the force that the film would exert on unit length of a barrier that was preventing it from spreading to a clean surface. (It is possible to carry through the calculation of the "adsorption isotherm", the relation of "coverage" to the *gas* pressure P, without having to make an explicit calculation of Π, which does not seem to be directly measurable.)

To complete this calculation, and to determine the precise form of the transcriptions that enable us to step from one problem to the other, we write down the "grand" partition function for the adsorption problem. The "ordinary" partition function is simply

$$\binom{N}{n}\exp\{(n\chi_0+\tfrac{1}{2}n^2\chi_1)/kT\}$$

because, for a given n, the energy is the same, but there are $\binom{N}{n}$ distinguishable ways of selecting n sites out of a total of N. (We are treating the adsorbed atoms as indistinguishable.) The grand partition function is therefore

$$\text{G.P.F.}=\sum_{n=0}^{N}\lambda^n\binom{N}{n}\exp\{(n\chi_0+\tfrac{1}{2}n^2\chi_1)/kT\} \tag{14}$$

which agrees exactly with expression (1) provided that we make the following transcriptions

$$\chi_1\rightarrow 4\mu^2\nu$$

$$kT\log\lambda+\chi_0\rightarrow 2\mu H-2\nu N\mu^2$$

together with a shift in the energy-zero of $N\mu H-\frac{1}{2}\nu N^2\mu^2$. On commonsense grounds, we have already decided that n/N is the analogue of θ, the "coverage". From the relation $\lambda=\exp(g/kT)$ we can determine g_{ads}, the partial potential per molecule in the adsorbed phase (which is

to be equated to g_{gas}, to determine the equilibrium). Now λ can readily be found from the analogue of equation (2), which is easily seen to be

$$kT(\log \lambda - \log n + \log (N-n)) + \chi_0 + n\chi_1 = 0 \qquad (15)$$

and the Fowler adsorption isotherm (1936) readily follows from this on using (11). The behaviour of such an adsorption isotherm (fig. 16) is quite analogous to the isotherm of a van der Waals gas. Below a certain temperature, corresponding to the Curie temperature in the magnetic case, there will be, at each temperature, a certain critical pressure at which the coverage can change discontinuously. For interactions corresponding to the antiferromagnetic case (adsorbed atoms *repelling* one another), no discontinuity in the isotherms is predicted at all.

The transcriptions that have to be made to pass from the magnetic to the adsorption problem are thus comparatively simple. We have already pointed out in Chapter II that the type of transition that can actually be observed depends on the constraints imposed by the physics of the problem as well as on the mathematical nature of the model used. No discontinuity occurs in the ferromagnetic Weiss model unless $H=0$. Since we cannot vary χ_0, we cannot produce an analogous situation in the adsorption problem *directly*, but we can do something that is *almost* equivalent, namely we can keep the temperature constant but alter the pressure in the vapour phase. Since the Gibbs functions per atom for vapour and adsorbed phases have to be equal for equilibrium, the effect on the adsorbed phase is almost the same as a change in the effective zero from which energies are measured. Analytically, this has practically the same effect as a variation of χ_0. The jump in coverage that occurs at a certain value of pressure, for any T below T_c, is thus the analogue of the jump from positive to negative I that occurs when H passes through zero. Corresponding to the fact that the jump is between magnetic intensities of equal absolute value is the fact that the jump in θ, the coverage, is from θ to $1-\theta$. Not many instances of this predicted phenomenon of "critical adsorption" seem to be known. Fowler (1936) compared his original theory with the data of Cockcroft (1928) on the adsorption of cadmium on copper, with reasonably satisfactory agreement. The theory was further developed by Roberts to cover cases

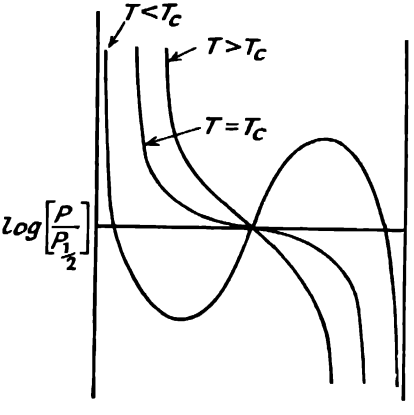

Fig. 16. Fowler's theory of adsorption.

where an adsorbed atom could "cover up" more than one site. The reader is referred to Roberts and Miller (1949) for a detailed account of this work. A phenomenon closely related to critical adsorption, the *solution* of hydrogen in palladium, will be described below (p. 134).

We are not at present concerned with a discussion of approximations such as (6), our object only being to show that such approximations can be readily *transcribed* to suit several situations. For the present we limit ourselves to the remark that, although such approximations apparently result from the assumption of an interaction of extremely long range, they *also* arise as crude first approximations to the consequences of an interaction *restricted to nearest neighbours only*, that is, interactions of extremely short range. (See p. 149.)

6.6. A simple Theory of Condensation of a Vapour

The transcription to enable us to discuss the condensation of a vapour is almost the same as that appropriate for the adsorption problem. The necessary transcriptions have been indicated by Yang and Lee (1952) for nearest-neighbour interaction, and by Temperley (1954) for long-range interactions. We suppose that a given vessel contains N "cells" of equal volume V/N, and that no more than one molecule may be in each cell. Some such assumption as this is necessary to take account of the repulsions between molecules, due to their finite size. To take account of their attractions at longer distances, we assign to each pair the energy $+\infty$ for two molecules in the same cell and $-\epsilon$ for two molecules in different cells. The grand partition function can be written down as for the adsorption case, and will be the same as expression (14), with χ_0 replaced by zero, and χ_1 by ϵ. The physical meanings of N and n in this new context are almost obvious, because, if V is the volume of the whole assembly, V/N is the volume of a cell ($=b$ say) which may contain not more than one molecule. n is the actual number of molecules present, so that V/n is v, the volume associated with one molecule. (The pressure associated with the gas phase in the adsorption problem has no analogue in this assembly. The pressure of the imperfect gas is, in fact, analogous to the "two-dimensional pressure" that we called Π in the adsorption problem, but did not calculate explicitly.) An explicit formula for the gas pressure can be derived at once by using the thermodynamic interpretation of the grand partition function, for a discussion and proof of which see Rushbrooke (1949).

$$PV = kT \log (\text{grand partition function}) \qquad (15)$$

Replacing expression (14) by its maximum term, inserting the value of λ given by (13), and making the transcriptions

$$\chi_0 \to 0, \qquad \chi_1 \to \epsilon, \qquad n \to V/v, \qquad N \to V/b$$

we obtain, for the equation of state of an imperfect gas according to this same crude assumption about the interactions between molecules,

$$P+\frac{a}{v^2}=-\frac{kT}{b}\log\left(1-\frac{b}{v}\right) \tag{16}$$

an equation which was derived directly from the simple Weiss model by Temperley (1954). As its consequences are very similar to those of the van der Waals equation itself, we shall not discuss them further here.

A point that does call for a brief mention is that we have apparently derived an equation allowing for metastable states by an absolutely rigorous treatment of a statistical-mechanical model. A similar remark applies to Fowler's adsorption isotherm, and will apply later on to most versions of the theory of solutions and of formation of superlattices. According to what we said in Chapter III (pp. 42–46) such a situation ought to be impossible, because a proper statistical mechanical average over *all* accessible states of an assembly can predict no more than *one* value of a quantity such as the pressure, for a given value of volume and temperature. It can be shown that this difficulty would *not* be removed by more rigorous evaluations of the asymptotic forms of series such as (14) considered as functions of n (instead of simply taking the maximum term as we have done here), but that it probably arises from a slightly incorrect method of proceeding to the limit of a large assembly. The reader is referred to Temperley (1954) for a discussion of this point, which does *not* affect the utility of the model that we have chosen to *illustrate* the process of transcription we are discussing. (It is probable, but not yet certain, that, if the passage to a very large assembly were done in an absolutely consistent way for this extreme long-range type of interaction, the discontinuities in the thermodynamic functions would remain as they now are, but that the metastable states would be eliminated.) The question of the possibility of allowing for metastable states without destroying the consistency of statistical mechanical treatments has already been discussed (p. 41).

6.7. The Theory of Solutions

A further transcription of equation (14) can lead to a simple theory of a two-component assembly with limited mutual solubility, equivalent to the derivations by quite a number of early workers. We shall suppose that the molecules are practically alike in size and shape, and that they only differ noticeably in that the interactions between like and unlike molecules are different. Once again, we recognise that theories of this kind are extremely crude first approximations. On this understanding, it is clear in the first place that, for a so-called "regular" solution (which satisfies the above conditions approximately and for which, in addition, it is a reasonable approximation to assume some sort of

quasi-lattice structure), the question of limited solubility can only arise if the interaction is such that like molecules prefer to be together. For the entropy is at a maximum when the two sorts of molecule are thoroughly well mixed, and, if this can be done at no cost in interaction energy, it is clear that there is no tendency to unmix.

Thus, the situation is the same as in the simple theory of liquids, for which we need *attractive* forces in order to cause a phase transition. Closer consideration shows that we can create a theory of solutions simply by replacing the assumptions that led to equations (14)–(16) by the alternative idea that we have, instead of n filled cells and $N-n$ empty ones (attractive forces then leading to the possible splitting of the assembly into two phases), just the following situation. N_A cells containing A-atoms, N_B cells containing B-atoms with $N_A+N_B=N$. In keeping with the type of assumption we made for the pure liquid, we assume for the number of distinguishable arrangements simply the number of ways of selecting the A-occupied cells, or $\binom{N}{N_A}$, while for the energy we assume a sum of terms proportional to N_A^2, N_AN_B and N_B^2 which can be reduced to a quadratic function of N_A by using the fact that N_A+N_B is constant. The resulting theory then becomes, formally, practically identical with that of the pure liquid. Phase-separation effects, associated with limited solubility, are to be expected if the coefficient of N_A^2 (in the energy thus transformed) is negative. (In the pure liquid theory, the coefficient of n^2 in the energy had to be negative.)

We shall not discuss such theories further here, as the consequences are given in detail by Rushbrooke, *Statistical Mechanics* (1949). We shall merely point out that, to get the grand partition function (for the solution) in the ordinarily accepted sense of the term, we must multiply the "ordinary" partition function

$$\binom{N_A+N_B}{N_A} \exp\{-(V_{AA}N_A^2+V_{BB}N_B^2+2V_{AB}N_AN_B)/\boldsymbol{k}T\} \quad (17)$$

by $\lambda_A^{N_A}\lambda_B^{N_B}$ and then sum over all possible values of N_A and N_B. In practice one keeps the volume fixed, and, for this very simple model in which each "cell" is definitely occupied by an A- or B-type molecule, this means that N_A+N_B is held constant. The sum to be calculated is then of just the same type as (14), but, instead of λ we have λ_A/λ_B. The further developments then depend on exactly what type of problem we are considering. If we are considering the equilibrium of a solution with a vapour phase, then we have to form the grand partition function and pick out the maximum term, which enables us to determine relations between λ_A, λ_B and the mean value of the ratio N_A/N_B, while λ_A and λ_B are equal to $\exp(g_A/\boldsymbol{k}T)$ and $\exp(g_B/\boldsymbol{k}T)$ and these are fixed by the

composition of the vapour phase. If, however, we are discussing the problem of mutual solubility, it is simpler to work with the "ordinary" partition function (17) keeping the ratio N_A/N_B fixed. The phenomenon of *limited mutual solubility* will then show itself if there is any value of the ratio N_A/N_B which makes (17) a *minimum*. If there is, then the assembly can *reduce* its free energy (and increase its partition function) by *splitting* into two phases of compositions *different* from this one. Again the reader is referred to Rushbrooke (1949) for details. (See fig. 17.) For each temperature, there are, in general, two such values of N_A/N_B, or none, and the plot of these values against T is usually called the "critical mixing" or "solubility" curve. See Hildebrand and Scott, *Solubility of Non-electrolytes* (1950), and Rushbrooke (1952) for reviews. One problem that seems to await solution is the existence of pairs of liquids such as triethylamine and water, which show mixing curves that are concave *upwards*, or nicotine and water, whose mixing curve is completely *closed*.

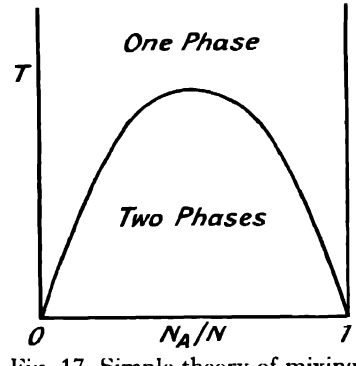

Fig. 17. Simple theory of mixing.

An interesting "analogue" of the critical adsorption phenomenon occurs with solutions of hydrogen in palladium. Although the treatment is formally very similar to that of critical adsorption there is, in fact, no doubt that hydrogen can actually reach the interior of heated palladium. Since one of the components is gaseous and the other solid, the ordinary experimental method of studying mixtures of liquids by measuring the pressure and composition of the vapour phase is hardly appropriate. It is better to plot a "solution isotherm" analogous to an adsorption isotherm—that is, we compute at each pressure the mass of hydrogen that is "missing" from the gas phase, this being the gas that is "dissolved" in the solid. Such a theory has been developed by Lacher (1937 a, b), on the basis of an equation very similar to (14), and, for this problem, it makes very little difference whether we use a simple theory of Fowler (1936) type or whether we attempt to improve it by a Bethe (1935) approximation. The isotherm shows discontinuous jumps in the solubility as the pressure is increased, in a manner quite similar to that of Fowler's adsorption isotherm. In this region of concentration, the existence of two phases can be detected by X-ray methods, because the lattice constant varies a little with the hydrogen content. Lacher's curves (1937 a, b) are in excellent agreement with the experimental work of Sieverts and Brüning (1932) and Gillespie *et al.* (1926; 1936)

and the predicted "metastable" regions, analogous to the metastable regions of vapour and liquid predicted by van der Waals's theory, also seem to be verified experimentally. See also Fowler and Guggenheim (1939).

6.8. The Theory of Superlattices

It may be verified, from what we have just said, that the question of limited mutual solubility does not arise in the present type of model unless like molecules prefer to be together, i.e. $V_{AA}+V_{BB}>2V_{AB}$, and one asks whether, in the opposite case, any other kind of discontinuous transition takes its place. The existence of the phenomenon of antiferromagnetism (p. 124) also leads one to ask whether any analogous phenomenon occurs for the assembly in which the total numbers of A and B molecules are held fixed. So far, such behaviour has been detected in only one type of assembly, the solid solution, which is the only case we consider explicitly here. It is probable, indeed almost certain, that analogous effects must occur in liquid solutions and in adsorption, but they would be hard to detect. For a discussion of the effects that may occur when adsorbed atoms repel one another, and of the indirect evidence that some sort of ordered pattern is probably formed in this case, the reader is referred to Roberts and Miller, *Adsorption of Gases on Solids* (1949). For a discussion of other co-operative effects in *films*, which seem to have quite as much variety as those in liquids, the reader is referred to Adam, *Physics and Chemistry of Surfaces* (1938).

The phenomenon that occurs in some alloys in which *unlike* atoms prefer to be together is known as *superlattice formation*, and is of the following type. At absolute zero, the two species of atom would try to sort themselves out into two sublattices in such a way that each atom is near to as many of the other species as possible. Various ways in which the atoms so sort themselves out are known, the actual pattern depending on the lattice type and on the relative numbers of each type of atom present. Usually, too, a certain type of superlattice will only form within a certain range of compositions. One of the simplest known cases is β-brass, which approximates to a Cu-Zn composition, and has a body-centred cubic structure. In the ordered state, the Cu atoms mainly occupy cube-corners and the Zn atoms cube-centres. However, matters are not always as simple as this, for example the alloy Cu_3Au has a face-centred cubic structure, and tries to order itself in such a way that the Au atoms preponderantly occupy *one* of the *four* simple cubic sublattices into which a face-centred cubic lattice can be divided. Again, the alloy Cu-Au tries to order itself into a layer structure. The prediction of such features as the arrangement of the sublattices is quite beyond the scope of any theory—indeed there is very little known about the relationship between the interaction function (even in a *pure*

substance) and the type of lattice that it forms. All that we can attempt to do is to take the observed lattice structure and type of superlattice as *data*, and simply attempt to follow the process of segregation of the two different types of atom into the two sublattices as the temperature falls. At high temperatures we have a "disordered lattice", i.e. the spatial structure is quite definite, but there is random mixing of the two types of atom. What we attempt to follow theoretically, and to compare with experimental data, is the progress with temperature of the "sorting-out" process. The "sorting-out" or "ordering" process is usually followed by X-ray analysis, but less precise information can also be obtained from the variation of electrical resistance, and from dilatometric measurements.

As we might expect, the relationship between the theory we are about to develop and the model of the antiferromagnetic described by equations (8) and (9) is going to be very similar to that between equation (17) and equation (1). In the "magnetic" case we had to consider all possible proportions of the two types of atom, and then to select from the partition function the term corresponding to the thermodynamically most profitable choice; in the "solution" case, the single term (17) that we must work with was prescribed for us in advance by the composition (assuming that the composition and temperature are such that a homogeneous phase can exist at all). In the present case, the partition function corresponding to equations (8) and (9) corresponds to a *double* series, summations being over all possible values of the variables n_1 and n_2. Prescribing the composition of the whole assembly imposes *one* condition relating these two so we shall not expect our new partition function to consist of just one term, but it will reduce to a *single* series each term of which will correspond to a different distribution of one type of atom between the two sublattices. (In the state of complete order, we shall have approached, as nearly as the composition of the assembly permits, to a state of affairs in which each of the two sublattices is occupied by only one type of atom.)

The partition function corresponding to assumptions such as (8) and (9) is of the form

$$f=\sum_{n_1}\sum_{n_2}\binom{N_1}{n_1}\binom{N_2}{n_2}\exp\{-E(n_1, n_2)/kT\} \qquad (18)$$

where $E(n_1, n_2)$ is a quadratic function of n_1 and n_2. We may not insert just *any* quadratic function here, (8) being the most general form of function that is permitted by the physics of the magnetic problem and by the type of interaction assumed. (It is clear that the *interaction* energy can involve only quadratic terms in M_1, M_2 and equally clear that M_1 and M_2 can appear linearly in the term $-H(M_1+M_2)$, but not in any other way.) We shall determine in a moment the corresponding

most general form for the energy in the order-disorder problem, but we must first determine the correct form for the partition function. If N_1, N_2, the numbers of "places" in the two sublattices are fixed, and N_A, N_B, the numbers of atoms of the two species in the whole assembly are also fixed, it is clear that the composition of one sublattice is fixed by that of the other.

Let r=number of A-atoms on sublattice 1. Then

$$N_1-r=\text{number of B-atoms on sublattice 1}$$
$$N_A-r=\text{number of A-atoms on sublattice 2}$$
$$N_2-N_A+r=\text{number of B-atoms on sublattice 2}$$

We are assuming, as usual, that there are no vacant sites, so that $N_1+N_2=N_A+N_B$. Then the proper partition function for this problem is

$$f=\sum_r \binom{N_1}{r}\binom{N_2}{N_A-r} \exp\{-E(r)/kT\} \tag{19}$$

where $E(r)$ is some quadratic function of r whose form remains to be settled. This can be done without much difficulty, though the argument is a little more subtle than in the magnetic case. We restrict ourselves to an alloy of a composition that will just "fit into" the sublattices, that is, we assume $N_A=N_1$, $N_B=N_2$, in order to avoid unnecessary complications. The generalisation to arbitrary composition presents little difficulty. (In practice, as we have seen, superlattice formation always occurs over a finite *range* of compositions.)

With a suitable choice of the function $E(r)$, we can follow the variation of $\bar{r}$ with temperature, for the equilibrium value of r will, as usual, be just that corresponding to the maximum term in (19). Instead of working with r directly, it is customary to use a closely related parameter S which we define as the degree of long-range order. We suppose that it is a linear function of r, and satisfies, in addition, the following two conditions:

(a) It is unity in the completely ordered state, that is, $r=N_A$ so that all the A-atoms are on sublattice 1.

(b) It vanishes in the completely disordered state, that is, when every one of the sites has the same probability, $N_A/(N_A+N_B)$, of being occupied by an A-atom, which implies that $r=N_A^2/(N_A+N_B)$.

The only choice of S that satisfies these conditions is

$$S=\frac{r(N_A+N_B)-N_A^2}{N_AN_B} \tag{20}$$

We now make the assumption, quite analogous to Weiss's assumption of an "effective field", that the gain of energy resulting from a small

increase in S is proportional to the value of S itself. This is obviously correct when we are near the state of complete disorder, because a slight change in any *completely random* arrangement of A- and B-atoms cannot result in any significant energy gain. On the other hand, if the ordering is nearly complete, rearranging a few atoms to increase S a little more must result in a relatively large energy-gain. The assumption

$$\partial E/\partial S \propto S$$

is thus nearly right at both ends of the range of values of S, and is the most general one we can make if we restrict ourselves to a *quadratic* form for the ordering energy. Integrating, we find that, if we take the energy of the completely ordered state as zero,

$$E=E_0(1-S^2) \tag{21}$$

We can now substitute expressions (20) and (21) into (19) and maximise with respect to S. For $N_A=N_B$ we get the very simple equation

$$\bar{S}=\tanh(\tfrac{1}{2}E_0\bar{S}/kT) \tag{22}$$

which is, formally, of exactly the same type as equation (2) for $2\bar{n}-N$ when $H=0$, and it will lead to a specific heat jump in exactly the same way, the Curie temperature being given by $2kT_c=E_0$, below which $\bar{S}$ gradually increases from zero, just like the spontaneous magnetisation in a ferromagnetic. For a discussion of the case when $N_A\neq N_B$, so that a more complicated equation for S replaces (22), the reader is referred to Fowler, *Statistical Mechanics* (1936), Chap. XIII. (See also p. 25.) The implicit equation for S has *three* positive roots, and jumps from zero to a finite value at the critical point (see fig. 18). The phase-change is now a *first-order* one and involves a latent heat. Unlike the van der Waals gas, the latent heat never vanishes except for the special case $N_A=N_B$ and remains finite even at the critical temperature itself. This is another instance of what we mentioned in Chapter II (p. 17), namely that the classification of a phase-transition might depend very much on the nature of the constraints imposed by the problem.

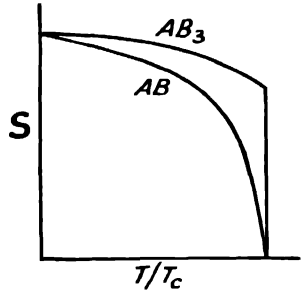

Fig. 18. Degree of order according to simple theory.

We have gone into this question of the transcription into one another of theories of physically different effects at some length because much waste of time and misunderstanding can be caused by a lack of appreciation of these basic facts, that there exists a set of theories that can each

be transcribed to suit a large number of different physical situations, but that the process of transcription requires a certain amount of care. Later in this chapter we shall introduce some approximations that are distinctly better than the Weiss theory and do at least take *some* account of the increase of the strength of the interaction as the distance between two systems decreases. These better approximations can also be applied to a large number of physical situations by the same type of transcripton.

6.9. The three Types of Pairs of Thermodynamic Variables

During our study of these very different, but related, physical problems, we have met pairs of extensive and intensive thermodynamic variables of three different types. We first have pairs such as volume and pressure, or magnetic moment and magnetic field, which are directly measurable and any of which can be held constant during a measurement. (In practice, the type of measurement in which M is held constant, H and T being varied together, is seldom made, but there is no reason why it should not be.) The second type of pair is illustrated by the variables A and Π in the adsorption problem. Π, the two-dimensional analogue of pressure, can, in fact, be measured for a film adsorbed on a *liquid* surface, by measuring the force on a barrier which prevents the film expanding on to a clean surface, these being the classical experiments of Lord Rayleigh. In such conditions it is practicable to work with a film containing a fixed quantity of matter, and to study the variation of A, or the reciprocal quantity θ, with Π. For an *immobile* adsorbed film on a solid surface it is, as we have seen, more practicable to measure the variation of θ with the pressure of the gas phase in equilibrium with the film. (In principle, Π might perhaps be measured as it should cause a slight variation in the average spacing of the adsorption sites, but this effect is probably extremely minute.) For a further discussion of immobile films (which are not always in true equilibrium), see Roberts and Miller, *Adsorption of Gases on Solids* (1949).

When we consider the variable S, the degree of order in an alloy, we have a variable that can definitely be measured, we have only to use X-rays of a wavelength such that the two types of atom in the alloy present appreciably different cross-sections of scattering. S can be made to vary by altering the temperature. Nevertheless, it does not seem to be possible, even in principle, to define a variable that is related to S in the same way that H is related to M in a magnetic body. The application of a field "takes hold of" the atomic magnets and orients them, but we have no analogous way of varying S. At a given temperature, it will attain an equilibrium value that is entirely determined by the temperature and composition (with a possible slight dependence on density or pressure), this equilibrium value giving a minimum of the

free energy as usual. If we *quench* an alloy, it can be obtained in a metastable state, but the corresponding energy can only be recovered as heat and the subsequent change of S cannot be made to do work. In contrast, a body such as a superheated liquid can easily be made to do mechanical work against the external pressure, but the "force" conjugate to S seems to be permanently zero. It will be also remembered that the form we assumed for the relationship between S and the energy contained no term linear in S. Thus, the "force" conjugate to a thermodynamic variable may (a) be measurable, (b) exist but not be measurable in practice, (c) have no objective existence.

Tisza (1949) has given an elaborate discussion of the modifications that have to be made in the thermodynamic treatment of phase-transitions if any such "internal" variables are involved. Formally, such a variable resembles an "ignorable co-ordinate" in mechanics, and, as long as we are concerned with equilibrium conditions only, all that we need do is to equate to zero the corresponding derivative of the free energy (or other appropriate thermodynamic potential), solve the resulting equation for S and then substitute the corresponding equilibrium value of S back into the free energy, or other thermodynamic potential, which then becomes the correct one for use with the remaining thermodynamic variables. In other words, such a variable is treated on the same *formal* footing as, for example, the occupation number of an elementary energy level. Such a number can conceivably be *measured* by an observation from outside the assembly, but possesses no conjugate *force* enabling it to be *influenced directly*, and its "equilibrium" value is determined by "selecting the most probable state", which is the same as maximising the entropy or minimising the appropriate thermodynamic potential.

Some writers have suggested that thermodynamically irreversible effects are *always* associated with changes in "internal" variables like S. If this statement is meant to apply only to variables such as S for which actual measuring procedures exist, then it is clearly false. (Consider, for example, the van der Waals gas, which undoubtedly shows irreversible effects, although no variables except P, V and T are involved.) If, on the other hand, the statement is meant to apply to *all* internal variables, even though they cannot be directly measured, then it would have to be applied to the occupation numbers themselves, and it then becomes a truism. (Clearly, no thermodynamic change at all, reversible or not, can take place without alterations in the mean occupation numbers.)

This existence of thermodynamic variables of these different types has helped to obscure the basic similarity of the mathematics underlying these different problems. For example, equation (22) is formally the same as equation (2) for $H=0$, and there is no particular difficulty

in picturing an analogy between S, measuring the percentage of atoms "in their right places", and M, measuring the percentage of "positive" magnets, but all attempts to think of a physical analogy for H fail, so that, for some considerable time, it was thought that the relationship between these various related theories was not very close. We recall that the relationships between the intensive variables in the various problems are, very often, not at all obvious.

6.10. Approximations due to Bethe and others

A long series of attempts to find approximations that represented the proper consequences of the Ising model reasonably well, and yet could be derived relatively easily, has enabled one to draw two conclusions. First, that the convergence of all such methods is comparatively slow, secondly, that a number of fundamentally different approaches do lead to mathematically equivalent answers, at all events at the level usually known as "Bethe's first approximation" (1935). Moreover, some of these methods are capable of being applied to complicated cases, for which they should give decent first approximations, pending the development of something better. It is therefore profitable to examine Bethe's model when applied to a simple problem, to compare it briefly with other methods, and to indicate how extensions of these other methods to more complicated cases can be made. The transcription of the same model to other physical problems is also made more readily when one of the alternative forms of Bethe's first approximation is used. In its original form, it does not lend itself at all well to these manœuvres, but it has the advantage that it can, in this form, be compared most readily with the Ising-type nearest-neighbour model that it was originally intended to represent.

We select for our application the order-disorder problem, because this necessarily involves two sublattices. In many problems, the two sublattices become equivalent. It is possible, as we saw (p. 136) above, to pass with comparative ease from problems such as antiferromagnetism or order-disorder, that involve *two* sublattices, to ones such as ferromagnetism or the theory of solutions, for which the two sublattices become equivalent. The reverse step, though possible, is less easy, and introduces many opportunities for making mistakes.

Basically, the method is as follows. We write down exactly the partition function for a single "central" site together with the interactions between this site and the z neighbouring sites in the lattice. The full lines in fig. 19 show the group of interactions we consider explicitly, for the case of a plane square lattice. We then attempt to allow for the fact that the z "outer" sites are all connected with one another by paths that run through the lattice from nearest neighbour to nearest neighbour, without ever passing through the central site. See dotted

lines in fig. 19. In fact, the mathematical reason why the nearest-neighbour model leads to a transition of co-operative type is this existence of infinitely many alternative paths between any two lattice sites. Thus, the probable occupations of any two "outer" sites are correlated with one another not only via the central atom, but also via various other possible paths. The interactions of the central atom with the "outer" sites are taken account of exactly, while the indirect effect of the "outer" atoms on one another is handled by a long-range approximation of Weiss type. The value of the extra interaction parameter so introduced is *not* adjustable, but, as we shall see in a moment, can be determined, in terms of the nearest-neighbour interaction, by the requirement that the theory must be self-consistent, that is, that the central and outer sites are equivalent to one another if the two sublattices are equivalent.

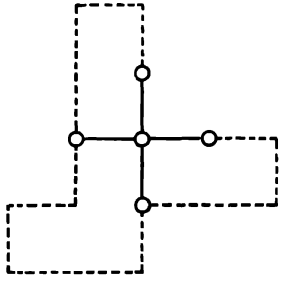

Fig. 19. Bethe's first approximation.

Bethe's second and third approximations consist of taking account explicitly of larger numbers of interactions, for example the second approximation would take account explicitly of the interactions shown in fig. 20 for the plane square lattice, the atoms consisting of the "centre", the "inner" group, whose interactions with the "centre" are considered explicitly, and the "outer" group, whose interactions with the "inner" group are considered explicitly, while the interactions of the "outer" group with the rest of the lattice are allowed for by means of the long-range type of approximation. Plainly, the process of successive approximations must eventually lead to exact results, but, as we have already mentioned, the convergence is disappointingly slow, and, for any solid lattice, it is hardly practicable to go beyond the second approximation. However, even the first approximation is valuable for at least three reasons:

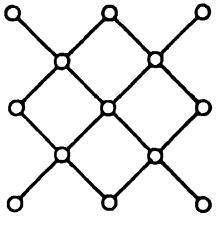

Fig. 20. Bethe's second approximation.

(a) It is undoubtedly a closer approximation to the consequences of an interaction between atoms that falls off with increasing distance than is the Weiss theory. In particular, it is a better approximation to the true consequences of the Ising model.

(b) It at least shows, in a crude way, how the consequences of an assumed interaction are likely to be related to the type of lattice, and to

the manner in which we split up the lattice into sublattices. A Weiss model altogether fails to give such information.

(c) Its consequences are undoubtedly in better agreement with experiment than are those of the Weiss theory, and at least one new effect (absent in the Weiss model) is predicted qualitatively.

We shall confine ourselves to the first approximation and to the simple case of two equivalent sublattices, e.g. the body-centred cubic lattice split into one sublattice consisting of the cube corners, the other comprising the cube-centres. We shall further suppose that all the nearest neighbours of a site in one sublattice lie on the other sublattice, and, for simplicity, that the two constituents are present in equal numbers. Quite a number of these assumptions may be dropped without seriously complicating matters, but a treatment of the face-centred cubic lattice in which some nearest neighbours of one site are nearest neighbours of one another is a difficult problem. Peierls (1936 b). For methods of applying the theory to more general cases, the reader is referred to Fowler and Guggenheim, *Statistical Thermodynamics* (1939), Chaps. VIII and XIII, and Guggenheim, *Mixtures* (1952). We first write down the partition function for a site in the a-sublattice, that is known to be occupied by an A-type atom. This site has z nearest neighbours in the b-sublattice, of which any number from 0 to z may be A atoms. We suppose that the Boltzmann factor for an unlike pair of nearest neighbours is unity, while that for a like pair is $\exp(-w/kT)$. Then we have:

All z neighbours of type B.
Boltzmann factor unity. Weight unity

$z-1$ neighbours of type B, one of type A.
Boltzmann factor $\exp(-w/kT)$. Weight z.

$z-r$ neighbours of type B, r of type A.
Boltzmann factor $\exp(-rw/kT)$. Weight $\binom{z}{r}$.

The "weight" of each distribution arises simply because r A-atoms may be selected out of a total of z possibilities in $\binom{z}{r}$ different ways. Summing for all possible values of r, we have for the partition function for an a-site known to be occupied by an A-atom the result $(1+e^{-w/kT})^z$. We take care of the effect of the more distant atoms on those in the "outer" sites by multiplying each term in this expression by ϵ for each A-atom on the outer sites, so that we now have $(1+\epsilon e^{-w/kT})^z$. If a site in the a-sublattice is known to be occupied by a B-atom the contribution to the partition function when there are $(z-r)$ neighbours of type B and r of type A is $\binom{z}{r}\exp\{(r-z)w/kT\}$, and we now introduce the same factor ϵ to allow for the effect of the more distant atoms

on the r A-atoms in the outer sites. Summing over all r as before we get $(\epsilon+e^{-w/kT})^z$ for the partition function for the a-site occupied by a B-atom, so that the complete partition function for the a-site is

$$f=(1+\epsilon e^{-w/kT})^z+(\epsilon+e^{-w/kT})^z \qquad (23)$$

the first term representing all possible cases when an A-atom is on the site and thus being a measure of the probability of this, while the second term describes all possible cases when a B-atom is on the site, and thus measuring *this* probability. (This method of choosing the parameter ϵ is characteristic of the Bethe theory. It may be necessary to introduce more than one such parameter when the neighbours of one site are nearest neighbours of one another, Peierls (1936 b).)

We shall now show that a simple consideration of self-consistency suffices to determine ϵ as a function of w/kT and z. For the method of constructing expression (23) was to introduce a factor ϵ whenever an A-atom occurred among the z "outer" sites, so that the probability that there are exactly r A-atoms on these sites (the occupation of the central site being unspecified) is simply proportional to the sum of the two terms involving ϵ^r in (23), and the *average number* of A-atoms on the z "outer" sites is obtained by multiplying these two terms by r, summing for all r, and then dividing by f. Thus we have, since the operation $\epsilon\partial/\partial\epsilon$ results in ϵ^r being multiplied by r, the result that the average number of A-atoms on group of z sites is

$$\epsilon\frac{\partial}{\partial\epsilon}(\log f)$$

the probability that a *specified* outer atom is an A-atom being just $1/z$ of this. To secure self-consistency in the case in which A- and B-atoms are present in equal numbers, it is necessary that the probability of finding an A-atom or an a-site is equal to that of finding a B-atom on a b-site. Since the central site has been supposed to be an a-site, the outer sites must be b-sites, so that

$$1-\frac{\epsilon}{z}\frac{\partial}{\partial\epsilon}(\log f)=\frac{(1+\epsilon e^{-w/kT})^z}{f} \qquad (24)$$

giving us an implicit equation for ϵ. The consequences of this equation may be reviewed fairly briefly. For fuller discussions, the reader is referred to the review article by Nix and Shockley (1938) or to Fowler and Guggenheim, *Statistical Thermodynamics* (1939).

(a) Equation (24) is *always* satisfied by $\epsilon=1$. From the way that this parameter ϵ was introduced, this solution would mean any given site is equally likely to be occupied by an A- or B-atom, i.e. the long-range order, S, is zero.

(b) Below a certain Curie temperature, which is given by $1-2/z = \exp(-w/zkT_c)$ there are *three* possible values of ϵ. One of them corresponding to an excess of A-atoms on the a-sites, another to a deficiency of A-atoms on these sites, and thus to an excess of A-atoms on the b-sites. This arises simply from the symmetry of the model (for clearly nothing is changed if we reversed the labels on all the sites).

(c) Values of ϵ differing from unity, when they exist, correspond to a more stable state than $\epsilon=1$. For a given value of ϵ, either side of equation (24) represents the probability of finding an A-atom on an a-site, and is thus equal to $2S-1$, by the definition of S, the long-range order.

(d) Even above the Curie temperature, although there is, on the average, no distinction between the two sublattices ($\epsilon=1$), it remains true that, if a certain site is known to be occupied by an A-atom, there will be a preponderance of B-atoms among its nearest neighbours (the "outer" sites in fig. 19), while the next ring of sites surrounding these contains, on the average a slight *excess* of A-atoms and so on. This situation is usually known as "local ordering", and exists at all temperatures. This effect is not predicted at all by a model of Bragg-Williams type, and is the analogue of the existence of the distribution function in a liquid (p. 53). If a molecule of liquid is definitely known to be within a certain small volume, then, in the immediate neighbourhood, the number of molecules to be expected per unit volume will be, at some places, greater than that corresponding to the mean density, while, at others, it will be less. In the simple model of a liquid that we had above (p. 131) no such effect appeared. This naturally raises the question whether, like the distribution function, the local ordering can be detected by X-rays. In principle this is possible, but, in practice, the small change in scattering predicted is hard to separate from "background" effects. For some recent work on this question see Wilchinsky (1944) and Cowley (1950 a, b).

(e) This persistence of local ordering at all temperatures also leads to a feature in the specific heat anomaly *not* predicted by a Bragg-Williams-type model, namely a "tail" in the specific heat curve extending over the entire temperature range above the Curie temperature. As was pointed out in Chapter II, such "tails" seem to exist for all known phase transitions, with the single exception of the superconductive transition, but the exact situation in the immediate neighbourhood of the transition temperature itself is always rather uncertain. (See fig. 21.)

(f) If we let $z\to\infty$ in such a way that zw remains finite we recover a theory of Bragg-Williams or Weiss type. In this limiting case the "tail" of the specific heat curve disappears. This suggests the possibility of allowing for the effect of the finite range of an actual interaction by defining an "effective number of neighbours", that is, by treating z

as an *adjustable constant* measuring the effective range of the interaction rather than as something fixed by the lattice type. A consideration not unlike this has been used by Néel (1934) in the magnetic case, but, in alloys, the approximate size of the "tail" is reasonably predicted by taking z as actually equal to the number of nearest neighbours.

(g) The agreement of the actual specific heat curves with the Bethe first approximation, though decidedly better than that with the Weiss model, is still rather poor. See Nix and Shockley (1938), Fowler and Guggenheim (1939). Comparison of the Bethe theory with the known exact consequences of the nearest-neighbour model in two dimensions indicates that the correct consequences of such a model in three dimensions are a "higher" and "thinner" anomaly than that given by the Bethe theory, which are changes of just the type needed to improve agreement with experiment.

Fig. 21. Specific heat anomaly, according to Bethe theory.

(h) We have already discussed above (p. 119) the influence of possible "side effects", such as a variation in the Debye Θ with the degree of order, and the effect of thermal expansion on the ordering energy which are, in principle, capable of improving the agreement also, but at present, there does not seem to be any means of deciding whether or not these effects are of major significance.

6.10.1. Approximations equivalent to Bethe's First Approximation

We give here a brief account of the two apparently different forms of approximations, which are, in fact, equivalent to Bethe's approximation, and are, at the same time, of such a nature that they can readily be generalised to more complicated problems. We consider again the model in which $\frac{1}{2}N$ sites are in one sublattice and each has, as nearest neighbours, z out of the $\frac{1}{2}N$ sites in the other sublattice. We suppose that there are a total of R A-atoms occupying sites on sublattice a. Now any pair of neighbouring sites will belong one to each sublattice, and each such site can be occupied in two different ways, by an A-atom or a B-atom. Let X be the total number of pairs of nearest neighbours of the type (Aa; Bb), by which we mean the number of pairs for which an A-atom is on an a-site, and a B-atom on a neighbouring b-site. Then we have the following distribution of atoms on sites:

R A-atoms on sublattice a	$\frac{1}{2}N-R$ B-atoms on sublattice a
$\frac{1}{2}N-R$ A-atoms on sublattice b	R B-atoms on sublattice b

We also have

$$(\mathrm{Aa};\mathrm{Bb})+(\mathrm{Aa};\mathrm{Ab})=\text{Total number of neighbours of the } R \text{ A-atoms on sublattice a}$$
$$=zR$$

Similarly

$$(\mathrm{Aa};\mathrm{Bb})+(\mathrm{Ba};\mathrm{Bb})=\text{Total number of neighbours of the } R \text{ B-atoms on sublattice b}$$
$$=zR$$

and

$$(\mathrm{Ba};\mathrm{Ab})+(\mathrm{Ba};\mathrm{Bb})=\text{Total number of neighbours of the } (\tfrac{1}{2}N-R) \text{ B-atoms on sublattice a}$$
$$=z(\tfrac{1}{2}N-R)$$

A fourth equation of this type also exists,

$$(\mathrm{Aa};\mathrm{Ab})+(\mathrm{Ba};\mathrm{Ab})=z(\tfrac{1}{2}N-R)$$

Using these equations, we find

$$\left.\begin{aligned}(\mathrm{Aa};\mathrm{Bb})&=z(R-X)\\(\mathrm{Aa};\mathrm{Ab})&=zX\\(\mathrm{Ba};\mathrm{Ab})&=z(\tfrac{1}{2}N-R-X)\\(\mathrm{Ba};\mathrm{Bb})&=zX\end{aligned}\right\} \qquad (25)$$

where X is a quantity that has to be determined in order that the number of pairs of different types can be fixed. It has to be determined, as usual, by making the partition function a maximum, and this, in turn, involves making some estimate of the statistical weight of a state of given X, though the interaction energy itself is precisely known as a function of X, since we are considering only interactions of nearest neighbours.

The problem of estimating the statistical weight of a state when N, X and R are given is unsolved for any three-dimensional lattice. We shall use an approximate combinatorial formula, due to Chang (1939) which turns out to be equivalent to Bethe's method. However, we shall here derive the combinatorial formula *ab initio*, as the derivation both indicates *why* the Bethe approximation fails to represent the accurate consequences of the nearest-neighbour model at temperatures near the critical, and also suggests means by which even better approximations can be obtained. A very crude assumption would be that of the "non-interference of pairs". This would imply that *pairs* of the four types, of a total number $\frac{1}{2}zN$, enumerated by equation (25), could be distributed about the lattice completely independently of one another, among $\frac{1}{2}zN$ "places". One might expect this to be valid, when X is small (state of nearly complete order), but it cannot possibly be correct when the number of pairs of all kinds are nearly equal (state of nearly complete

disorder). A-A and B-B pairs *can* be distributed nearly independently of one another when their total numbers are small so that two such like pairs will only rarely be close to one another. As X becomes larger, close encounters between like pairs become more and more likely, and the assumption that the probabilities of occupation of a given pair of sites by like or unlike pairs are independent of what is happening on neighbouring sites becomes less and less satisfactory. Indeed, if X is large, the assumption of "non-interference" grossly over-estimates $g(N, R, X)$ the statistical weight of a state of given X, and we shall try to correct this fault.

This can be readily seen, as follows: The assumption of "non-interference" would lead to the following expression for $g(N, R, X)$:

$$\frac{(\frac{1}{2}zN)!}{((zX)!)^2\{z(R-X)\}!\{z(\frac{1}{2}N-R-X)\}!}=h(N, R, X) \quad \text{(say)} \qquad (26)$$

For a fixed R, this attains a maximum value when $X=R(N-2R)/N=X_0$ as can be shown in the usual way by using Stirling's theorem and differentiating, but the true value of $g(N, R, X)$, summed over all X for a given R, is precisely known. This sum must be equal to the number of ways of distributing R A-atoms amongst $\frac{1}{2}N$ sites and $(\frac{1}{2}N-R)$ B-atoms amongst $\frac{1}{2}N$ sites or $\left\{\binom{\frac{1}{2}N}{R}\right\}^2$ which is much *less* than the maximum value of expression (26), because the expression we have just obtained refers to the "parcelling out" of N "things", while expression (26) refers to the "parcelling out" of $(\frac{1}{2}zN)$ "things". (As usual, $\sum_X g(N, R, X)$ is practically identical with $g(N, R, X)_{\max}$.)

Thus, the proposal is that we should, at least, make our approximation correct in the region of nearly complete disorder, and this can be done, by writing, instead of (26),

$$g(N, R, X)\approx\left\{\binom{\frac{1}{2}N}{R}\right\}^2\frac{h(N, R, X)}{h(N, R, X_0)} \qquad (27)$$

where $h(N, R, X)$ and $h(N, R, X_0)$ are given by (26). The energy associated with given values of R and X, is, using expressions (25) for the numbers of nearest-neighbour pairs of various types,

$$\begin{aligned} E(N, R, X)&=\{z(R-X)+z(\tfrac{1}{2}N-R-X)\}V_{AB}+zx(V_{AA}+V_{BB}) \\ &=\text{constant}+zX(V_{AA}+V_{BB}-2V_{AB}) \qquad (28) \\ &=\text{constant}+2zXw \end{aligned}$$

where w is the increase of energy resulting from replacing an unlike by a like pair of nearest neighbours.

The consequences of the combinatorial formula (27) can now be worked out without further approximations. We combine (27) with

(28) and sum over possible values of X and R to form a partition function. This sum can be handled by the standard process of searching for the maximum term. We maximise first with respect to X, keeping R constant, then substitute for X in (27) and (28) and maximise with regard to R, thus getting the equilibrium value of R, which is related to S, the long-range order, by a linear relationship in the manner explained earlier (p. 137).

Maximising with respect to X gives us the following equation for $\overline{X}$, the most probable value of X according to (26), (27) and (28),

$$\frac{(R-\overline{X})(\frac{1}{2}N-R-\overline{X})}{\overline{X}^2}=\exp\left(\frac{2w}{zkT}\right) \tag{29}$$

We refer the reader to Rushbrooke (1938) for a formal proof that the equilibrium value of X that follows from (29) really does, when substituted back into (27) and (28), the partition function afterwards being maximised with regard to R, imply results precisely the same as those of Bethe's first approximation. For the appropriate generalisations to the cases of non-equal sublattices and non-equal percentages of the components A and B, see Fowler and Guggenheim, *Statistical Thermodynamics* (1939), Chap. XIII. There are, however, two features of equation (29) that call for some comment. In the first place we notice that, if we let $z\to\infty$ keeping zw finite, the right-hand side of equation (29) is equal to unity. We then have $\overline{X}=X_0$, where $X_0=R(N-2R)/N$, and, using (27) and (28), we find for the partition function

$$f=\sum_{R}{}'\left\{\left(\frac{\frac{1}{2}N}{R}\right)\right\}^2\exp\left\{\frac{-E_0R(N-2R)}{NkT}\right\} \tag{30}$$

where $E_0=\lim_{z\to\infty}(2zw)$, which form of partition function, the energy being a quadratic function of R, has already been repeatedly discussed as a consequence of theories of Weiss or Bragg-Williams type. Such theories can thus be thought of either as *rigorous consequences* of interactions of *extremely long range*, or as *crude approximations* to the proper consequences of the *nearest-neighbour* model.

6.10.2. The "Quasi-chemical" Type of Approximation

A second feature of equation (29) that also calls for comment is the following: Using expressions (25) we may write (29) as an "equilibrium" condition determining the most probable numbers of the four different types of pairs of atoms that can occur on the lattice, thus

$$\frac{(\mathrm{Aa};\,\mathrm{Bb})(\mathrm{Ab}:\,\mathrm{Ba})}{(\mathrm{Aa};\,\mathrm{Ab})(\mathrm{Ba};\,\mathrm{Bb})}=\exp\left(\frac{2w}{zkT}\right) \tag{31}$$

which may be compared with the law of mass action for reacting gases, the "reactants" being the four possible types of pair thus:

$$\mathrm{Aa};\ \mathrm{Bb}+\mathrm{Ab};\ \mathrm{Ba}\rightleftharpoons\mathrm{Aa};\ \mathrm{Ab}+\mathrm{Ba};\ \mathrm{Bb}$$

Equation (31) resembles closely the equation governing the equilibrium of a double decomposition chemical reaction of the type

$$PQ+RS\rightleftharpoons PS+RQ$$

occurring in a closed vessel so that the total numbers of the various types of atom present were all fixed. Such an assembly has only one degree of freedom and therefore needs only a single reaction constant to fix its condition completely. The analogy might be pushed even further, because, in such conditions, the "reaction constant" should be a function of the temperature alone, and an analogous result is true for equation (31).

It does not seem to be possible to push the "chemical analogy" to a point at which we can infer the actual form of the "reaction constant", so that, for this, we have to rely on some other form of the theory, either the Bethe approximation or the combinatorial formula. Nevertheless, the fact that the Bethe approximation can be put in the form (31) has proved of great value. It naturally leads one to ask whether it might not be fruitful to consider "chemical equilibrium" between larger groups of atoms, say, for example, between the sixteen different types of groupings of four atoms on groups of four sites. In the plane square lattice one might consider a square of four sites, in a three-dimensional lattice a tetrahedron of sites. The generalisations that have been carried out have been along two distinct lines.

(a) Attempts to obtain results, perhaps of the same order of accuracy as that of Bethe's first approximation, applicable to more complicated assemblies, such as solutions in which the solute and solvent molecules differ in size and shape, solutions of molecules such as polymers and rubber-like molecules of "chain" type, adsorption problems in which the adsorbed molecule "covers up" more than one adsorption site. Many such applications have been made, some of which would have been difficult or impossible to find if the theory had stayed in Bethe's original form. For accounts of this work the reader is referred to Barker (1953); Guggenheim (1952), *Mixtures*; Miller (1949), *Solutions of High Polymers*; Roberts and Miller (1949), *Adsorption of Gases on Solids*.

(b) The second type of generalisation has been to seek for alternative means of improving Bethe's first approximation into something more closely resembling the consequences of the nearest-neighbour model, now that it has become clear that attempts to apply Bethe's own process of obtaining better approximations have not been very successful. The

reasons have been mentioned already, the laboriousness of the first, second, third ... approximations increasing almost exponentially, while the convergence towards the final result is very slow. This exasperating behaviour also occurs when attempts are made to obtain series expansions of the partition function in terms of suitable variables, as we shall see later. Since one knows that, in other branches of physics, a series can often be changed from slow to rapid convergence by some transformation of the variable or other mathematical "trick", we shall be constantly on the look out for possible "short-cuts" in this field.

For the remainder of this chapter, we shall be concerned with attempts to collect information about precise consequences of the nearest-neighbour model rather than with comparisons with experiment of approximations that, in the neighbourhood of the transition region, are certainly no more than qualitative representations of the correct consequences of the nearest-neighbour model. The reader who is interested in such comparisons is referred to Nix and Shockley (1938), and Fowler and Guggenheim, *Statistical Thermodynamics* (1939), Chap. XIII, and, for solutions, Guggenheim, *Mixtures* (1952). It should always be remembered that many of these comparisons and deductions were made at a time when it seemed as if Bethe's first and second approximations were both fairly close to the exact consequences of the nearest-neighbour model, and the tendency was to conclude that this model was itself only a rough approximation to the truth. This matter has already been discussed above (p. 117).

The comparisons did, however, serve at least one useful purpose. An extremely interesting point can be made about these approximations. We consider Bethe's approximation, in which the effect on a particular atom of a few of the atoms in its immediate surroundings is allowed for explicitly, while the indirect effect of the remainder is allowed for by an assumption of "effective-field" type. Bethe's approximation in fact represents some compromise between the consequences of "short-range" and "long-range" interactions. In fact, no interactions that actually occur are of these extreme types, and it is natural to ask: "May not a 'compromise' approximation like Bethe's be a *reasonable representation of some interaction of a kind not too far removed from what exists in practice*?" ("What exists in practice" is, almost certainly, an "ordering interaction" which could be represented by a function of distance $f_{AA}+f_{BB}-2f_{AB}$, the energy gain or loss on changing two like pairs of atoms into unlike pairs keeping the distances constant. The *difference* between these three terms probably decreases fairly rapidly with increasing distance, even if one of the f's by itself does not.) *A priori*, it would have been possible to hope that, "if we were lucky", one of these approximations would be roughly equivalent to some

interaction falling off with distance according to a law not too far removed from what occurs in practice. If such a thing *has* happened by a "fluke" (or if it happens in the future with some other type of approximation), there would not be nearly so much point in spending time and labour on the present line of approach, which is, first, to determine the correct consequences of the nearest-neighbour model, so that the comparison between theory and experiment can at least *begin* on a secure foundation, secondly, to attempt to improve this model.

It is not known for certain whether any of Bethe's or similar approximations *do* in fact represent with any closeness the true consequences of some interaction that falls off smoothly with distance, but their comparison with experiment seems to show that, even if any of them do, the interactions that they so represent are not very close to physical reality, that is, that the hoped-for "lucky fluke" has not yet happened! However, considering the immense amount of labour that has already been spent on gaining information about the nearest-neighbour model, and the very wide variety of problems to which one could apply information of this kind if it ever became available (information, that is, that the consequences of a *particular* interaction function were represented with good accuracy by a simple type of partition function), it is obviously well worth while to keep on watch for the possible occurrence of such a "fluke". From this point of view, it is certainly worth comparing any new method of approximation with experiment.

6.10.3. Generalisations of the Quasi-chemical method. The Approximations of Hill and Kikuchi

We shall compare the results of the quasi-chemical method, in which only *pairs* of adjacent atoms are considered, with two more complicated treatments, those of Hill (1950) and Kikuchi (1951) in which "equilibria" between larger groups of atoms are considered. We shall consider the two-dimensional plane square lattice in the absence of a magnetic field (or the equivalent adsorption problem in which half the sites are occupied) and shall calculate the entropy as a function of energy, that is, of the total numbers of nearest neighbours. The correct variation of entropy with energy is known for this model as a result of Onsager's work (1944) and has been computed by Prigogine, Sarolea and van Hove (1952) and compared with Chang's formula (1939), the latter representing the consequences of the Bethe first approximation. The results of this comparison make it immediately apparent that the "corrected hypothesis of the non-interference of pairs", on which formulae such as (27) are based, leads to the correct value of the entropy only in conditions of nearly complete disorder (or small or zero spontaneous magnetisation). The "uncorrected hypothesis",

which would lead to taking such an expression as (26) for the statistical weight, should, on the other hand, give the correct answer for a state of nearly complete order, or magnetisation nearly to saturation. Thus, the introduction of the "normalising factor" in (27), has undoubtedly improved the approximation to $g(N, R, X)$ in the region of maximum entropy, but only at the expense of *impairing* it at the other end of the range of values of the order.

Since the very process that these models are trying to trace is the change in the order and entropy with temperature, it is, in view of Prigogine, Sarolea and van Hove's comparison (1952), not surprising that the general description of the transition region, e.g. height of specific heat anomaly and position of Curie temperature, given by Bethe's approximation is a poor representation of the true consequences of the model while, at the same time, quantities such as the "free energy of mixing" are reproduced well. The reason for the latter circumstance is plain; by the time the percentage inaccuracy in the entropy has become serious the entropy itself is small, and the percentage inaccuracy in the free energy is much less than that in the entropy itself.

Obviously, there is no uniquely specified process for generalising the quasi-chemical method once we begin to consider groups larger than pairs, and the two formulae now to be mentioned are only representatives of a large number of possibilities. After consideration of equilibrium between the sixteen possible types of groups of four sites, Hill (1950) suggests the following as likely to be reasonably satisfactory for a total of N sites:

$$g \approx \frac{(Nx_1)!(Nx_2)!}{[(Nz_1)!\{(Nz_2)!\}^4\{(Nz_3)!\}^4\{(Nz_4)!\}^2\{(Nz_5)!\}^4(Nz_6)!]^{1/2}(N!)^{1/2}} \quad (32)$$

Kikuchi (1951), used a somewhat more complicated argument, in which he considered "equilibrium" between single atoms, pairs, groups of three atoms and groups of four atoms, finally arriving at the result (the notation used in these formulae will be explained in a moment).

$$g \approx \frac{\{(Ny_1)!\}^2\{(Ny_2)!\}^4\{(Ny_3)!\}^2}{(Nx_1)!(Nx_2)!(Nz_1)!\{(Nz_2)!\}^4\{(Nz_3)!\}^4\{(Nz_4)!\}^2\{(Nz_5)!\}^4(Nz_6)!} \quad (33)$$

The corresponding result using the Chang combinatorial formula, for the case where the two sublattices are equivalent, reads

$$g \approx \frac{N!(2Nx_1{}^2)!(2Nx_2{}^2)!((2Nx_1x_2)!)^2}{(2Ny_1)!((2Ny_2)!)^2(2Ny_3)!(Nx_1)!(Nx_2)!} \quad (34)$$

the notation being that of Kikuchi's paper (1951) and is as follows:

x_1, x_2 represent the respective probabilities that any given site is occupied in the two possible ways, e.g. A and B atoms, + and − magnets, "occupied" and "empty";

y_1, y_2, y_3 represent the relative probabilities that any neighbouring pair of sites is occupied in the three possible ways AA, AB or BA, BB respectively;

z_1 to z_6 represent the relative probabilities that a given square of four sites are occupied in the respective manners shown in fig. 22;

where, for example, z_2 includes all four of the configurations

AA	AB	BA	AA
AB	AA	AA	BA

($x_1=x_2=\frac{1}{2}$ is the only case for which we have exact information from Onsager's work). These quantities are, of course, not all independent, for we have, as conditions of consistency,

$$\left.\begin{aligned} x_1+x_2&=1\\ y_1+y_2&=x_1\\ y_2+y_3&=x_2 \end{aligned}\right\} \tag{35}$$

$$\left.\begin{aligned} z_1+2z_2+z_3&=y_1\\ z_2+z_3+z_4+z_5&=y_2\\ z_3+2z_5+z_6&=y_3 \end{aligned}\right\} \tag{36}$$

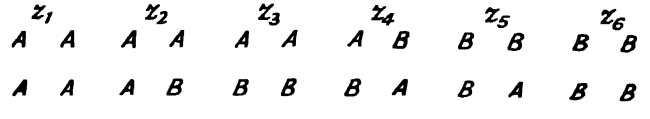

Fig 22. Illustrating Kikuchi's notation.

The interaction energy is proportional to $y_1+y_3-2y_2$ and, assuming various values of this quantity, the y's are determined by (35). The corresponding entropies, according to the two approximations (32) and (33), can then be calculated. We have to choose the z's to make g a maximum, subject to the three restrictions (36).

In Table I, the results of such calculations are given, and compared with the figures given by Prigogine, Sarolea and van Hove (1952) for the exact model and for the "pairs" approximation (34). It will be seen that both (32) and (33) are decidedly better than (34). These approximations have been checked in various other ways. Kikuchi (1951) shows that the consequences of (33) are, in fact, analytically the same as those of an entirely different type of approximation (the best approximate result hitherto known) of Kramers and Wannier (1941). The latter

authors shows that the problem of the plane square lattice could be reduced to an eigenvalue problem, in a manner that will be indicated below (p. 160), and they devised a variational method for solving this problem. It is not yet clear whether the agreement between their result and that of Kikuchi (1951) is fortuitous, or whether there is some deep reason for it.

TABLE I. THE PLANE SQUARE LATTICE

Comparison of various approximate treatments with exact results due to Onsager (1944) and Prigogine, Sarolea and van Hove (1952). Calculated values of $g(\nu)$, where $(g(\nu))N$ is the number of configurations containing $N\nu$ unlike pairs of nearest neighbours, and the number of A and B atoms is each $\frac{1}{2}N$. For the plane square lattice ν varies from 0 to 2. $g(\nu)$ is symmetrical about $\nu=1$.

$\nu=$	0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
"Quasi chemical"	0·50	0·75	0·96	1·15	1·37	1·54	1·70	1·82	1·91	1·98	2·00
Hill (1950) .	0·71	0·92	1·09	1·27	1·44	1·59	1·73	1·86	1·94	1·99	2·00
Kikuchi (1951) .	1·0	1·13	1·25	1·37	1·49	1·61	1·72	1·82	1·91	1·98	2·00
Exact* (1952) .	1·0		1·31	1·44		1·69		1·88		1·99	2·00

(*From calculations by Prigogine *et al.*)

Another check on approximations (32) and (33) can be made as follows. Since these approximations are based on specifying the relative abundances of different configurations of four sites forming a square, one can apply them both to discussing a model in which *second-nearest* neighbour interactions are also considered, that is, interactions are allowed along the diagonals of the squares. As one alters the relative strengths of these interactions, the position of the Curie point will vary (actually reaching absolute zero when the interaction between second nearest neighbours is in the antiferromagnetic direction and numerically half as strong as that between nearest neighbours, Domb and Potts (1951)). Hill (1950) has computed the behaviour of the Curie temperature in terms of the strengths of the two interactions, and a similar calculation has been made by Temperley (unpublished) using Kikuchi's approximation (33). These results can be compared with those of Domb and Potts (1951) on the same model, using the series expansion method, and comparisons have also been made of the initial susceptibilities (susceptibility when the magnetic field is zero) for various ratios of the two interactions. The agreement is in all cases comparable with the probable inaccuracies of the various approximations, so detailed results will not be given. Kikuchi's approximation (1951) is correct for both complete disorder and complete order, and thus seems to be slightly better than Hill's (1950). Both the Hill and the quasi-chemical

approximations formally give a statistical weight of *less than unity* for the ordered configuration. Such results (calling for negative entropy!) are physically absurd. Since the position of a critical or Curie temperature is fixed by a balance of energy and entropy, the failure of such approximations to locate the transition temperature properly is completely explained.

While both of these approximations (32) and (33) appear to be better than Bethe's approximation, there is no obvious way of improving either of them further. Kikuchi (1951) reports that he has tried analogous methods on other lattices, and that he finds that a small increase in the size of the group (for example taking a group of six instead of four in the square lattice) does not necessarily result in any worth-while improvement. Since Kikuchi's approximation for the square lattice has turned out to be equivalent to that of Kramers and Wannier (1941) the reader is referred to the latter paper for a comparison of the consequences of this approximation with results obtained by various other methods. Both (32) and (33) are open to the criticism made by Kramers and Wannier, namely that they fail to give the correct analytic behaviour of the specific heat near the Curie point (now known to be a logarithmic infinity for the plane square lattice). The result that the specific heat could *not* be discontinuous had already been found by Kramers and Wannier in 1941 by a method to be described below (p. 160).

6.11. The Approximations of Cowley and Zernike

Cowley (1950) has suggested a relatively simple approximate method which can be applied to any lattice. It is difficult to compare directly with the theories we have just been considering, because it completely neglects certain correlation effects that most of the workers in the field have considered to be of vital importance. The nature of the neglected correlation effects can best be seen by considering Zernike's theory (1940), who seems to have been the only other worker who has ventured to base a first approximation on complete neglect of these correlation effects. He attempted to allow for them by a process of successive approximations, but the theory then becomes extremely complicated, and, even in its final form, certainly does not represent a good approximation to the correct consequences of the nearest-neighbour model. The reader is referred to Kramers and Wannier's paper (1941) for a comparison of Zernike's results with those of other theories.

Zernike (1940) began by defining the parameter $p_{h,k,l}$ for the simple cubic lattice which is the probability that the atom at the lattice point (h, k, l) is an A-atom. On the basis that such probabilities as $p_{h,k,l}$, $p_{h+1,k+1,l}$ . . . are *independent* probabilities, one can set up a difference equation relating them, by means of the Boltzmann factors, to the strength of the interactions between nearest neighbours, thus

$$p_{h,k,l}=\frac{e^{6w/kT}}{1+e^{6w/kT}}p_1p_2p_3p_4p_5p_6+$$
$$\frac{e^{4w/kT}}{1+e^{4w/kT}}\{(1-p_1)p_2p_3p_4p_5p_6+p_1(1-p_2)p_3p_4p_5p_6+\ldots\} \quad (37)$$

where $p_1 \ldots p_6$ refer to the nearest neighbours of site (h, k, l). If we write $2p_i-1=r_i$, so that $r_i=0$ corresponds to the state of complete disorder, equation (37) becomes, to a first approximation when the r's are small,

$$r_{h,k,l}=n(T)(r_1+r_2+r_3+r_4+r_5+r_6) \quad (37a)$$

$r_1 \ldots r_6$ referring to the six nearest neighbours of (h, k, l), while $n(T)$ is a known function of temperature.

This equation is readily solved by using trial functions of the type $e^{i\lambda_1 h}$, $e^{i\lambda_2 k}$, $e^{i\lambda_3 l}$, where the possible choices of λ_1, λ_2, λ_3 are fixed, as usual, by the boundary conditions. Thus, this equation already gives indications of the existence of a transition temperature, and the mathematical reason for its existence is similar to that for the change in form of the solutions of the equation $(\nabla^2+n^2)\psi=0$ from "oscillatory" to "exponential" types as n^2 changes sign. An *oscillatory* solution for the $r_{h,k,l}$ corresponds to the existence of "long-range order", an *exponential* type to "local order only", but, strictly speaking, either type of solution implies *some* correlation between probabilities such as $r_{h,k,l}$ and $r_{h+1,k+1,l+1}$, a fact which has to be allowed for by successive approximations.

Cowley (1950) begins by assuming a quite general interaction energy between pairs of atoms at all distances (though he concludes later that the interaction energy *does* fall off very rapidly with distance, as a result of comparing his theory with experiment). He then splits up the lattice into shells of atoms surrounding the origin at various distances and then defines "short-range order parameters" α_i, such that, if m_A, m_B are the relative proportions of A- and B-atoms, $\alpha_i=1-p_i/m_A$, where p_i is the probability that an atom in the ith shell is an A-atom if the origin is known to be a B-atom. If there are c_i atoms in this shell, $c_i m_A(1-\alpha_i)$ of them will, on the average, be A-atoms, and the number of ways they can be arranged in the shell is

$$\binom{c_i}{c_i m_A(1-\alpha_i)} \quad (38)$$

if we assume that the A-atoms in each shell are completely uncorrelated.

Cowley now proceeds to assume that the entropy of the entire assembly, in which it is specified only that there is a B-atom at the origin, can be obtained by multiplying together one such factor (38) to take care of each shell, that is, he completely neglects indirect

correlation effects between atoms in different shells, by treating the different α_i's as completely independent, while the form of the assumption (38) is really equivalent to treating the arrangement of atoms *within* the ith shell as *random*. On the basis of these assumptions, the calculation can be carried through completely, the equilibrium values of the α_i's being determined by the thermodynamic condition that changing the atom at the origin from a B-atom to an A-atom must leave the free energy stationary. On the basis of the assumptions that we have made, the resulting changes in interaction energy and entropy are both known in terms of possible changes in the α_i's, and, if these really can vary *independently*, we can deduce a set of equations determining their equilibrium values. For any assumed variation of the interaction energy with distance these can be solved by successive approximation.

The limiting behaviour of the α's at the large distances determines the long range order S. For a 50 per cent A-B alloy we should have $\alpha_i \to \pm S^2$ (the upper or lower signs operating according as i is even or odd). For such a lattice, we get for S, the equation

$$\log\left(\frac{1+S^2}{1-S^2}\right)=\frac{2T_cS^2}{T} \qquad (39)$$

This implies that S varies as $(T_c-T)^{1/4}$ just below the Curie temperature whereas the Bragg–Williams and Bethe theories imply that S varies as T_c-T. In both cases, the energy associated with the long-range order is proportional to S^2 but in the Cowley model, as distinct from that of Bragg and Williams, we have an *infinite* specific heat, which, just above the Curie temperature, drops discontinuously to a small finite value, this, as in Bethe's theory, being associated with the short-distance order.

Cowley (1950) makes a comparison of his theory with the observed long-range order as a function of temperature for the alloys CuZn and Cu_3Au, and correctly remarks, in addition, that all the approximate theories give too low a value for the height of the specific-heat anomaly. He could also have mentioned that his predicted variation of specific heat just below the Curie temperature, as $(T_c-T)^{-1/2}$, is in good accord with the experimental findings, Sykes and Jones (1936 a, b), Moser (1936). He has also compared the predicted variation in local order in the first three shells with experiment, Wilchinsky (1944), Cowley (1950 b), and again the agreement is satisfactory. On the other hand, the following must be pointed out on the debit side:

(a) If Cowley's method were used as a "theory of the nearest-neighbour model", all more distant interactions being taken as zero, reference to his Table I (1950 a) shows that the theory gives much too high a value for the Curie temperature in terms of the interaction

energy. The ratio kT_c/E_0 is *higher* than those given by nearly all the approximate theories, all of which are themselves known to give values that are higher than the correct consequence of the nearest-neighbour model. In Cowley's (1950) comparison with experiment, T_c is treated as the adjustable quantity, so this difficulty is not apparent, but it is plain that the theory is *not* the *correct* consequence of the *model assumed*.

(b) Cowley's estimate of the entropy of disorder is certainly too high because of the neglect, already discussed, of various correlation effects. Just how bad is this sort of error is one of the very things that the more elaborate theories are trying to estimate in simple cases. It must be remembered that it *may* be possible to change the entropy-function considerably without vitiating all the results. For example, if we refer again to the Bethe model, equation (29) (though not equation (30)) would follow equally well whether we used the crude estimate (26) for the entropy, or the more correct one (27).

We thus incline to the view that the excellent agreement with experiment that Cowley (1950) finds must be due to the fortunate mutual cancellation of various errors, though his model undoubtedly helps one to gain insight into the relationship between "long-distance" and "local" ordering, which is not at all easy to follow in Bethe's model. Also, the *possibility* that some, as yet unknown, mathematical fact may permit one, in certain circumstances, to neglect correlations between parameters such as the α_i's and yet get sensible physical results cannot be overlooked. We have already met this sort of situation before, a crude approximation working much better than it has "any right" to do, in discussing the possible reasons for the success of the van der Waals model of a gas (pp. 61–64).

6.12. Kirkwood's Method

As a final example of theories that "got off to a promising start", then got bogged down by difficulties of computation, we may mention Kirkwood's method (1938). The method, or its equivalent, has been used in a few other problems, and may be capable of further applications. It is based on a very simple result in statistical mechanics, namely that the free energy can be written

$$F=-kT\log f=-kT\log\left[f_\infty+\sum_r\{\exp\left(-\epsilon_r/kT\right)-1\}\right]$$

where the ϵ_r's each represent the energy of one particular configuration of the lattice and f_∞ is the limiting value of the partition function at very high temperatures. Thus

$$F=-kT\log f_\infty-\frac{1}{kT}\sum_r\epsilon_r+\frac{1}{2(kT)^2}\sum_r(\epsilon_r)^2-\frac{1}{6(kT)^3}\sum_r(\epsilon_r)^3+\ldots \quad (40)$$

where the sums are to be taken over all possible ϵ_r's. This result can be

expressed in various other forms. Suppose now that we wish to determine the variation with temperature of some parameter such as S, the long-range order. We need only to determine the unweighted sums $\Sigma(\epsilon_r)^n$ over all possible states of the assembly corresponding to a specified value of S, the different "states" here corresponding to different possible arrangements of A- and B-atoms on the lattice. Kirkwood showed how to determine the first three of these sums as functions of S, and we can then determine the equilibrium value of S by minimising the free energy. As in the Bragg–Williams theory, we then have an implicit equation for S.

Fowler and Guggenheim (1939), Chap. XIII, claim that, since the terms in the partition function actually calculated by Kirkwood (up to the term $\Sigma(\epsilon_r)^3$) agree with those that result from the Bethe or quasi-chemical method, one ought to say that the Curie temperature and specific heat anomaly are the same for both forms of the theory. In practice, Kirkwood's method is usually reported as giving a somewhat "higher" and "thinner" specific heat anomaly than Bethe's approximation, in better agreement both with experiment and with what are now known to be the correct consequences of the nearest-neighbour model, so this criticism seems somewhat pedantic. In practice, it is difficult to lay down any *precise* rules for solving an *implicit* equation when it really consists of an infinite series of which only the first few terms are known. Whatever procedure one adopts, one cannot avoid making *some* concealed assumption about the form of the unknown higher terms. This difficulty becomes more and more serious as the temperature is lowered. A similar difficulty is discussed by Tredgold (1953).

6.13. Operator Methods. Series Expansions

We conclude this list of theories with an account of the principle by which some of these problems have been reduced to that of finding the largest characteristic value of an operator. For a few lattices this further problem can be solved in closed form and information obtained about the partition function, the spontaneous magnetisation or long-range order, and the short-range order as functions of temperature, Onsager (1944), Kaufman and Onsager (1949), Newell (1950 a, b), Houtappel (1950), Husimi and Syozi (1950), Temperley (1950), Wannier (1950), Syozi (1951). For some others, the operator problem cannot be completely solved, but can be handled by standard perturbation methods, starting from some case where the answer is known, such as zero or infinite temperature, Domb (1949 a, b). It is also possible to proceed by direct counting of the configurations on the lattice which correspond to different numbers of like or unlike neighbours, van der

Waerden (1941), Wakefield (1951). In a few such cases, enough terms of the series for the partition function or spontaneous magnetisation are known to enable reasonable guesses about such matters as the location of the Curie point to be made, but in others, the behaviour of the series is decidedly irregular and no such deductions can be made, van der Waerden (1941), Ashkin and Lamb (1943), Domb (1949), Brooks and Domb (1951), Domb and Potts (1951), Trefftz (1950), Rushbrooke (1952), Tanaka, Katsumori and Toshima (1951).

For an account of the methods that have been successful in obtaining exact results, the reader is referred to a review article by Newell and Montroll (1953), while the information available from series expansions has recently been summarised by Rushbrooke (1952).

A formal expression for the partition function can always be written down quite easily, taking advantage of the fact that each atomic magnet has only two states, which we represent by $\mu_j = \pm 1$. Its interaction with an external field is then described by $\exp(K\mu_j)$ or $\cosh K + \mu_j \sinh K$, if $\exp(\pm K)$ represent the Boltzmann factors describing the magnet in its two states. With a suitable convention about the zero of energy, the interaction of two atoms, j, k, with one another can be described by $\exp(H\mu_j\mu_k)$ or $\cosh H + \mu_k\mu_j \sinh H$, e^H representing the Boltzmann factor when both magnets are positive or both negative, and e^{-H} the Boltzmann factor when they are unlike. If one magnet is interacting simultaneously with an external field, and with other nearby atoms, it is readily verified that all possible configurations are automatically allowed for simply by multiplying together such factors, one for each interaction. Thus, for the general case of magnets being exposed to a magnetic field, and with interactions extending out to all distances, we should have

$$f = \sum_{\mu=\pm 1} \prod_{j,l} \exp(K\mu_j) \exp(H^{(l)}\mu_j\mu_{j+l}) \qquad (41)$$

the $H^{(l)}$'s varying with l in a manner determined by the variation of interaction with distance, and the summations being over the two possible values, ± 1, of each of the μ's.

Only very slight progress has been made with *direct* attacks on an expression such as (41). From now on, we confine ourselves to the case of no magnetic field ($K=0$). If we imagined the factors in expression (41) each expressed in the form $\cosh H + \mu_j\mu_k \sinh H$ and then the whole product multiplied out, the process of summing over $\mu_j = \pm 1$ would remove all terms containing μ_j to an odd power. In fact, the only types of term that would contribute anything are those corresponding to products of cosh terms multiplied by products of sinh terms corresponding to *closed paths* drawn on the lattice, a factor such as $\mu_j\mu_k \sinh H$ corresponding to joining the points j and k. The only lattices for which any exact results have been obtained are those of the special type which

possess a "topological dual". By this we mean that it must be possible to arrange the atoms in the lattice in such a way that all the possible "links", corresponding to terms such as $\mu_j\mu_k \sinh H$, can be arranged in such a way that they *do not cross* except at lattice points. For an account of the dual transformation of Kramers and Wannier (1941), and of the information about the partition function that can be obtained from it, the reader is referred to the review article by Wannier (1945). A method, actually using the properties of determinants in order to count the closed paths of various lengths, which is probably applicable to all lattices that possess a dual, has been suggested by Kac and Ward (1952), see also Newell and Montroll (1953). They have applied it to the plane square lattice, thus obtaining an expression for the partition function agreeing with that of Onsager (1944).

In practice, however, most of the known results have been obtained by making the summations called for by expression (41) one at a time in some special way, which reduces the problem to an eigenvalue one. We shall outline the "principle of partial summation" on which such derivations are based.

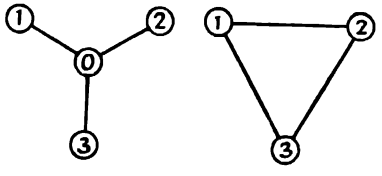

Fig. 23. Star-triangle transformation.

The process can be illustrated by considering the "star-triangle" transformation described by Wannier (1945). By it we can remove from a lattice any magnet that is bonded to others by not more than three "links" (fig. 23). The factors in the partition function associated with these three links $\mu_0\mu_1$, $\mu_0\mu_2$, $\mu_0\mu_3$ are

$$(\cosh H+\mu_0\mu_1 \sinh H)(\cosh H+\mu_0\mu_2 \sinh H)(\cosh H+\mu_0\mu_3 \sinh H) \tag{42}$$

We are supposing, for simplicity, that all three "links" are of equal strength H. If magnet μ_0 is not interacting with any other atoms, μ_0 will not appear anywhere else in the partition function, and the summation over its possible values ± 1 can be performed at once. Multiplying out and performing this summation, we obtain, as the contribution to the partition function from these three factors,

$$2 \cosh^3 H+2(\mu_1\mu_2+\mu_1\mu_3+\mu_2\mu_3) \cosh H \sinh^3 H$$

which may be factorised into

$$M(\cosh L+\mu_1\mu_2 \sinh L)(\cosh L+\mu_2\mu_3 \sinh L)(\cosh L+\mu_1\mu_3 \sinh L) \tag{43}$$

the two expressions agreeing provided that

$$M(\cosh^3 L+\sinh^3 L)=2 \cosh^3 H$$

$$M(\cosh L+\sinh L)\cosh L \sinh L=2 \cosh H \sinh^2 H$$

which can always be solved for M and L for any H. This means that the three interactions described by (42) *can be replaced* by the three interactions described by (43), provided that an appropriate factor M is introduced into the partition function. When more than three "links" meet, this process breaks down, because, if we introduced a fourth factor involving μ_0 into (42), the resulting expression, after summation, can no longer be factorised into terms representing interactions between *pairs*.

We must therefore proceed somewhat differently. As an illustration, consider the plane square lattice, which we imagine built up, row by row, by factors of the type given in expression (42). We imagine that the summations, $\mu_i = \pm 1$, have already been performed over the configurations of all magnets in row A (fig. 24) and previous rows. Let the magnets in row B be described by $\mu_1, \mu_2, \mu_3, \ldots$ and the corresponding ones in row C by $\mu_1', \mu_2', \mu_3', \ldots$. If the lattice were to be stopped at

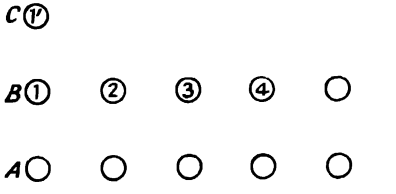

Fig. 24. Building up the plane square lattice.

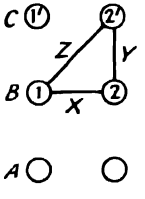

Fig. 25. Effect of two non-commuting operators.

row B, we should proceed as follows. First sum an expression such as (42) over $\mu_i = \pm 1$ for row A and all previous rows. This would leave us with an expression $\phi(\mu_1, \mu_2, \mu_3, \ldots)$ where the atoms in row B are still specified explicitly. To stop the lattice at row B we should simply sum ϕ over both possible values of each of $\mu_1, \mu_2 \ldots$, and the result would then give us the partition function. If, however, we want to add on another row, we first take account of interactions between the magnets in row B and row C, by multiplying ϕ by the factors in (42) representing the interactions between these rows, then sum over all possible configurations of row B (these magnets have now had *all* their interactions allowed for and are therefore "finished with"), finally we take account of interactions between the magnets *in* row C by multiplying by the factors in (42) representing interactions within row C. This will leave us with some expression $\psi(\mu_1', \mu_2', \mu_3', \ldots)$ involving the configurations of row C only, and we are ready to add another row.

We thus have the following result. The effect of adding row C and then summing over all possible configurations of row B has been to

change the expression $\phi(\mu_1, \mu_2, \mu_3, \ldots)$ to $\psi(\mu_1', \mu_2', \mu_3', \ldots)$ and it is this relation that we are going to express in operator form. If we can determine the form of this operator, we can infer the effect on the partition function of adding more and more rows simply by applying this operator repeatedly to a function such as $\phi(\mu_1, \mu_2, \mu_3, \ldots)$. In the limiting case, when the number of rows becomes very large, the effect on ϕ is practically equivalent to a multiplication by $\lambda^n_{\max}$, where n is the number of rows added, and $\lambda_{\max}$ is the largest eigenvalue of the operator.

We examine the effect of merely adding magnet μ_1' in row C, afterwards summing over $\mu_1 = \pm 1$ in row B. Since $\mu_1^2 = 1$ it follows that, whatever function ϕ may be, it can always be expressed as

$$\phi = f(\mu_2, \mu_3, \ldots) + \mu_1 g(\mu_2, \mu_3, \ldots) \tag{44}$$

where f and g are both independent of μ_1. We now introduce the factor $(\cosh H + \mu_1\mu_1' \sinh H)$ to take care of the interaction between magnets 1 in row B and 1′ in row C. Now sum over $\mu_1 = \pm 1$. The effect of this is to change ϕ into

$$\begin{aligned}\chi &= \sum_{\mu_1 = \pm 1} (f \cosh H + \mu_1 g \cosh H + \mu_1\mu_1' f \sinh H + \mu_1' g \sinh H) \\ &= 2f \cosh H + 2\mu_1' g \sinh H\end{aligned}$$

This relationship may be expressed by means of the operators $\mathbf{I}$ and $\mathbf{C}_1$ which are defined by

$$\mathbf{I}: 1 \to 1, \quad \mu_1 \to \mu_1', \qquad \mathbf{C}_1: 1 \to 1, \quad \mu_1 \to -\mu_1' \tag{45}$$

in the form

$$\chi = (e^H \mathbf{I} + e^{-H} \mathbf{C}_1)\phi \tag{46}$$

and thus we have determined the combined effect of *adding on another magnet, and at the same time summing over both configurations of the magnet it is interacting with in the preceding row*. This fact, that the operators involving $\mathbf{C}_1$, $\mathbf{C}_2$, etc., really each summarise the final result of *two* steps, first putting in an interaction and then performing a summation over the two configurations of the magnet that is "finished with", has not been sufficiently emphasised in the literature. Thus, in equation (46), ϕ describes the magnets in row B, while χ describes the *different* set of magnets (1′, 2,3,4,. . .).

In Onsager's treatment (1944) we add a whole row at once, *also* summing over configurations of the whole preceding row, which is equivalent to applying the operator

$$(e^H \mathbf{I} + e^{-H} \mathbf{C}_1)(e^H \mathbf{I} + e^{-H} \mathbf{C}_2)(e^H \mathbf{I} + e^{-H} \mathbf{C}_3) \ldots$$

This, by itself, is of course not the complete effect of adding a new row, because we have still to take account of the effect of the interactions of

magnets 1′, 2′, 3′ in row C with one another. This is taken care of by introducing the appropriate factors

$$(\cosh H' + \mu_1'\mu_2' \sinh H') \ldots$$

or by operating with

$$(\cosh H' + \mathbf{S}_1'\mathbf{S}_2' \sinh H') \ldots$$

where H' represents the strength of the interactions between neighbours in the same row, and $\mathbf{S}_1'$ is the operator: $1 \to \mu_1'$; $\mu_1' \to 1$, that is, it simply amounts to multiplying by μ_1'. Thus, we have shown that the effect of adding a complete row, summing over the preceding one and then taking account of the interactions in the new row can be represented by Onsager's operator. For methods of determining its eigenvalues and other properties reference must be made to the original papers, Onsager (1944), Kaufman and Onsager (1949).

Other workers, e.g. Kramers and Wannier (1941), Domb (1949), Newell (1950 a, b), have preferred to work with the operator corresponding to adding just *one* magnet at a time, on each occasion summing over two configurations of just *one* other magnet. Thus, Onsager's operator is readily shown to be equivalent to

$$[(\exp \mathbf{S}_1\mathbf{S}_2H')(e^H\mathbf{I} + e^{-H}\mathbf{C}_1)T]^m$$

where T is an operator with a "screw" property thus:

$$T\mathbf{S}_jT^{-1} = \mathbf{S}_{j+1}, \; T\mathbf{C}_jT^{-1} = \mathbf{C}_{j+1}$$

m being the number of atoms in a row, and $m+1$ being reckoned as 1, so that $T^m = 1$. Various actual representations of T in operator or matrix form can be given.

The fact that we have introduced an operator $\mathbf{C}_1$, which *anticommutes* with $\mathbf{S}_1$, arises from the fact that the operator $\mathbf{C}_1$ involves a summation over the two configurations of magnet 1, an "irreversible" step. Once we have applied an operator involving $\mathbf{C}_1$ we have for ever lost our chance of introducing further interactions with magnet 1 in row B, and all subsequent operations (until the operator $\mathbf{C}_1$ occurs again) will refer to magnet 1′ in row C, and so on. Once this position is fully realised, we can drop the primes in an equation such as (45). Such functions as ϕ, χ, ψ are then formally expressed in terms of the same μ's although they all three of them refer to three different sets of magnets. We can do this on the understanding that the set of magnets actually described by a "wave-function" such as ϕ, χ, ψ is not changed by applying any operator $\mathbf{S}_r$, but that the application of any operator containing $\mathbf{C}_r$ automatically results in our attention being transferred to a magnet one step higher up in the rth column.

The physical meaning of the anticommutation between these two

types of operator now becomes evident. An operation such as $\exp(H'\mathbf{S}_1\mathbf{S}_2)$ will refer to different *pairs of atoms* according as it is applied *before* or *after* $(e^{H}+e^{-H}\mathbf{C}_2)$. Thus, in fig. 25, is shown the effect of the operator

$$\exp(H'\underset{X}{\mathbf{S}_1\mathbf{S}_2})(e^{H}+\underset{Y}{e^{-H}}\mathbf{C}_2)\exp(H'\underset{Z}{\mathbf{S}_1\mathbf{S}_2}) \qquad (47)$$

The operation X being applied before Y, while Z follows Y. This operator was used by Newell (1950) in conjunction with a "screw" operator in his discussion of the plane triangular lattice.

Onsager (1944) has pointed out another aspect of this non-com-

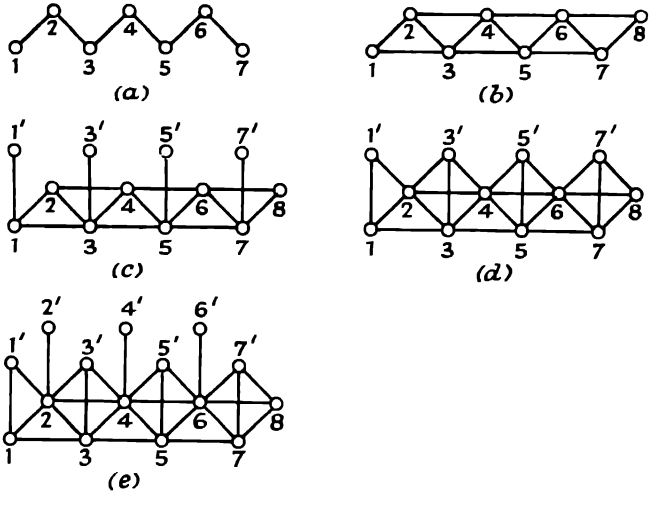

Fig. 26. Plane square lattice with second neighbour interactions.

mutation of operators. For the plane square lattice we can arrange them as follows

$$\ldots \mathbf{C}_1,\quad \mathbf{S}_1\mathbf{S}_2,\quad \mathbf{C}_2,\quad \mathbf{S}_2\mathbf{S}_3,\quad \mathbf{C}_3,\quad \mathbf{S}_3\mathbf{S}_4,\quad \mathbf{C}_4,\ldots$$

where each operator in this series anticommutes just with its two neighbours and commutes with all the others, all of them being square roots of unity. It could not make any difference to the eigenvalues of Onsager's operator if these basic operators were replaced by others with the same algebraic properties, in particular the cyclic transformation

$$\mathbf{C}_1\rightarrow\mathbf{S}_1\mathbf{S}_2\rightarrow\mathbf{C}_2\rightarrow\mathbf{S}_2\mathbf{S}_3\rightarrow\ldots \qquad (48)$$

must leave the partition function invariant. But the operators involving $\mathbf{C}_1$ contain e^{H} and e^{-H}, while those involving $\mathbf{S}_1\mathbf{S}_2$ contain $\cosh H'$ and $\sinh H'$, so the transformation (48) relates the partition function of this lattice to that of another square lattice in which we replace $\tanh H'$ by e^{-2H} and vice versa, which is precisely the dual transformation of

Kramers and Wannier (1941). The fact that it can be applied to all lattices that possess a topological dual is established by Wannier (1945), by an "elementary" argument.

We conclude by writing down the operator corresponding to the plane square lattice with second-nearest-neighbour interactions, both because the form of this operator does not seem to have been explicitly published before, and also because it is the "next problem on the list", as it is the simplest lattice for which the partition function is not known in closed form. A solution of this operator problem would be of great physical interest, for example one would like to know whether any new physical or mathematical features are introduced by the fact that the lattice does not have a dual. In comparing the known results for square, hexagonal and triangular lattices, the only new physical feature introduced in the triangular lattice is due to the existence of closed circuits containing an odd number of "links". The symmetry between the partition functions for "ferromagnetic" and "antiferromagnetic" interactions that exists in the square lattice is thus destroyed, certain triangular lattices in which two (or all three) of the interactions are antiferromagnetic actually having no Curie point at all, and a *finite entropy* at $T=0$, Wannier (1950), Houtappel (1950).

We build up the operator for the plane square lattice with diagonal interactions in a somewhat unconventional fashion, the rows being numbered, and the build-up taking place in the directions of the *diagonals* of the squares. Thus, if the magnets in a "row" are numbered as in fig. 26 (a) we first have the operator

$$\prod_j \exp\,(H'\mathbf{S}_j\mathbf{S}_{j+1}) \tag{49}$$

to take care of the interactions along the sides of the squares. Then (fig. 26 (b)) we introduce the operator $\prod_j \exp\,(H\mathbf{S}_j\mathbf{S}_{j+2})$ to take care of the interactions along the horizontal diagonals. We then move forward one step (fig. 26 (c)) along the *odd-numbered* vertical diagonals, at the same time taking care of the interactions along them, by means of the operator

$$\prod_j (e^{H}+e^{-H}\mathbf{C}_{2j+1})$$

We then apply again the operator (49), which, this time (fig. 26 (d)), describes interactions between the magnets 1′, 2, 3′, 4, etc. Finally we move forward along the *even-numbered* vertical diagonals (fig. 26 (e)) by means of the operator $\prod_j (e^{H}+e^{-H}\mathbf{C}_{2j})$, which brings us to the same situation as we had for the preceding row just before we added the interactions represented in fig. 26 (a). Thus, the complete effect of adding a whole new row is represented by the operations

$$\prod_j \exp(H'\mathbf{S}_j\mathbf{S}_{j+1})\prod_j \exp(H\mathbf{S}_j\mathbf{S}_{j+2})\Pi(e^{H}+e^{-H}\mathbf{C}_{2j+1})$$
$$\prod_j \exp(H'\mathbf{S}_j\mathbf{S}_{j+1})\prod_j(e^{H}+e^{-H}\mathbf{C}_{2j}) \quad (50)$$

applied in this order. We have distinguished between interactions along the sides and diagonals by means of the symbols H' and H respectively, but it *would* be possible to generalise the work to the case of all six interactions in a fundamental square being different.

It is fairly clear that the theory of operators such as (50), which represents a generalisation of Dirac's matrices and Eddingtons E-numbers, is at a fairly early stage of development. A big advance was made by Kaufman and Onsager (1949) by showing that the process of finding eigenvalues could, in the cases at present solved, be much simplified by spinor analysis.

6.14. Irreversible Effects associated with these Phenomena

We defer until the next chapter the discussion of irreversible effects associated with ferromagnetism. The methods of obtaining experimental information on adsorption make it difficult to decide whether irreversible effects occur or not, as an experimenter would often be inclined to reject an adsorption isotherm if it did not reproduce itself satisfactorily for rising and falling pressures. There are, however, some extremely interesting effects that can occur as a result of a film being *immobile*, but these hardly come within the category of changes of state. For an account of them the reader is referred to Roberts and Miller, *Adsorption of Gases on Solids* (1949). The phenomenon of *critical* adsorption, which *is* a genuine phase transition, does not ever seem to have been studied under *true* equilibrium conditions, so there is no means of deciding whether it occurs reversibly or not. The transitions that occur when certain films adsorbed on *liquid* surfaces are compressed are genuine phase transitions, analogous to those of a liquid or gas, and the reader is referred to N. K. Adam (1938) for an account of them.

A wide variety of irreversible effects occur with solutions. The phenomenon of *supersaturation* is widespread, and can often be made the basis of very spectacular experiments. As we have seen, elementary theories of solutions will predict such occurrences as "natural" consequences, in precisely the same way that the van der Waals or similar theories predict superheating for a pure liquid. As with pure liquids, it seems likely that a proper extension of statistical mechanics, on lines already discussed at length above (p. 41), can justify the acceptance of the predictions of metastable states by these "simple" theories. The part that "nucleation" plays in the recrystallisation of a solution is a well-established experimental fact, and experiments can be

devised in which crystallisation can be started or stopped at will. We are therefore on much surer ground than we are for pure liquids, where the very nature of the nuclei is still uncertain, so that the process of, for example, the explosion of a superheated liquid, once started, cannot be stopped or controlled. A similar remark applies to the supercooling of water below its freezing point, where again we do not know the nature of the nuclei.

The study of irreversible effects occurring in association with the limited solubility of metals in one another, together with the phase transitions that occur when an alloy is "annealed", "quenched" or "normalised", forms no small part of the science of metallurgy. Some typical transitions, and the associated irreversible effects are discussed in *Phase Transformations in Solids* (1951) to which the reader is referred. Successful attempts have been made, and are there described, to set up physical criteria that enable one to predict whether a certain transformation is likely to be "slow" or "fast", and to interpret various other details, but this field of enquiry seems to be at an early stage of development.

We have already referred to the time-effects that may occur in association with the order-disorder transition (p. 33). It seems extremely likely that the reason why such transitions have not been noted more often is that they require atoms within the lattice to exchange places, and the energy associated with this will usually be many times larger than the energy ultimately gained as a result of the interchange. From the work on melting (p. 97) one is inclined to conclude that such interchanges would perhaps not be very frequent unless one were reasonably close to the melting point of the alloy, and this may well mean that the phenomenon is suppressed in some cases, simply because one would have to go very near the melting point for the disordering or ordering process to occur at a reasonable rate. Compare the co-operative effects that occur with long-chain paraffins (p. 240). It has also been suggested by Borelius (1934) that some transitions are metastable or sluggish because of the existence of "free energy-barriers". Just as in the van der Waals theory of a liquid (and probably indeed for all mechanisms of transition), a finite *barrier of free energy* is to be expected for *any* transition that involves a latent heat. Indeed, it is an observed fact, Bragg and Williams (1934; 1935), that the Cu-Zn transition, which does *not* involve a latent heat takes place far more rapidly than the Cu_3-Au transition which *does*.

Precise information about these transformations is hard to obtain, because, unlike solid solutions, the transition does not lead to any *visible* changes in the alloy, and all the information about its progress is indirect. Nevertheless, a number of inferences about this *can* be made, and the reader who is interested cannot do better than turn to

the papers by Bragg and Williams (1934; 1935) and Sykes *et al.* (1936; 1937).

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CHAPTER VII

Ferromagnetism and Antiferromagnetism

7.1. Introductory

The ferromagnetic transition has been the most studied of all, both because of its technical importance and because its existence has been known for a very long time. As has already been mentioned, the Weiss (1907) theory of ferromagnetism is undoubtedly a satisfactory first approximation, and there seems little doubt that Heisenberg's (1928) explanation of the "molecular field" in terms of quantum mechanics is, in substance, correct. The real difficulty has been to find satisfactory ways of extending a treatment of Heisenberg's type, in which one begins with one magnetic element (spinning electron) bound to each positive ion in the crystal lattice. The required extension must be made in such a way as to take care of certain features of actual ferromagnetics. The following seem to be the main ways in which the theory has to be developed before it can be considered really acceptable:

(a) It must take account of the fact that all ferromagnetic atoms contain several valency electrons.

(b) It must take account of the fact that the "valency" electrons in a free atom correspond closely to the "conduction" electrons in a metal, though the correspondence is often not complete.

(c) The so-called "superexchange" mechanism, by which alignment of the spins of two electrons can occur as a result of the fact that they are both interacting with a third, really ought to be considered (Kramers (1934)).

(d) The theory ought to explain why ferromagnetism only occurs in a few pure metals and a few classes of alloys.

This is quite a formidable list of requirements, and it is perhaps not to be expected that a single unified theory should deal with them all. The main theories that exist at present seem to be as follows:

(a) Various refinements of the Weiss-Heisenberg conception of atomic magnets bound to a lattice-site.

(b) The collective-electron conception of Stoner (1938) which results as a natural development of the very successful Brillouin-Bloch theory of metallic conduction. Here the electrons responsible for ferromagnetism are considered to be those *in the conduction bands*, and thus free to move through the lattice.

(c) Bloch's (1930) development of Dirac's (1929) approximation treatment of systems containing a large number of spinning electrons.

All three of these theories have existed for some years, and each one of them seems specially adapted for describing certain aspects of ferromagnetism, but no method of synthesising them seems in sight at present. In recent years all three of them have been subjected to a most searching scrutiny, and a great many experimental and theoretical arguments have been put forward in support of particular points of view. The resulting controversy has been of the fruitful kind that has, in the past, often preceded some fresh fundamental advance in a subject (like the elaborate discussions about the ether that came immediately before the theory of relativity). The author's personal view is that all three theories survive in principle, but that there seems to be no doubt that all of them are capable of improvement in matters of detail. In this chapter, these theories will be briefly explained and an attempt will be made to summarise some of the criticisms that can be made of their weak points. The reader who wishes to pursue these matters further is advised to turn to the papers presented at the Washington Conference on Magnetism (*Rev. mod. Phys.*, Jan. 1953, especially the papers by Zener and Heikes, Slater, Wohlfarth, van Vleck and Smoluchowski, pp. 191 228). For a discussion of the possible range of validity of theories of the Bloch type, see also Wohlfarth (1949), Herring and Kittel (1951).

As has already been mentioned in Chapter VI (pp. 117–21), the number of experimental facts available of an "intrinsic" nature, that is, giving such information as the variation of the spontaneous magnetisation with temperature, or of susceptibility with temperature, is not at present large enough to enable us to "decide" between various theories, and some of the experimental findings can be "explained" on the basis of several different hypotheses. Many experiments in the past have concentrated on collecting information about particular materials under particular conditions of heat-treatment, and the details of a magnetisation curve are so dependent on secondary effects, that, although it may be possible to "analyse" them in terms of an assumed theory of the origin of spontaneous magnetisation, they throw little direct light on whether the theory is correct or not. Besides accounting for the existence of spontaneous magnetisation (remanence), considerable headway has been made in accounting for irreversible effects associated with ferromagnetism, such as coercivity and the Barkhausen effect. This progress was almost entirely due to Becker and his collaborators, see, for example, Becker, *Problem der Technischen Magnetesierungskurven* (1938), Becker and Döring, *Ferromagnetismus* (1939), Bozorth, *Ferromagnetism* (1951). The theory, in its present form, seems capable

of interpreting a wide variety of hysteresis effects, those that occur in technical materials as well as those occurring under the special experimental conditions that favour the appearance of very large Barkhausen domains. Although one or two ideas, such as the idea that domain walls may possess inertia as well as their other properties (see p. 214), have been added by later workers, it seems that a substantial amount of ground has been securely won. "Domain theory", as it now stands, seems unlikely to be substantially modified by any foreseeable changes in the fundamental theory of ferromagnetism, provided only that the essential idea of exchange interaction is retained in some form. Thus, magnetic hysteresis is one of the few irreversible effects associated with phase-changes that is understood fairly well, and it is interesting that a proper theoretical treatment of it has required consideration of the interplay of three or four quite distinct effects (exchange interaction, magnetic interaction, magnetic anistropy and magnetostriction).

A wide variety of irreversible effects besides true hysteresis also occurs in ferromagnetics, such as time effects, and thermal hysteresis. While progress has been made in interpreting them, they are not nearly so well understood as is true hysteresis. The reader is referred to the later chapters of Becker and Döring, *Ferromagnetismus* (1939), for a discussion of them.

7.2. The Exchange Energy in Quantum Mechanics

No progress beyond Weiss's (1907) theory would have been possible without some explanation of the very large interaction energies that have to be assumed between electrons in order to predict ferromagnetism at the transition temperatures actually found. A very simple computation shows that, by themselves, magnetic interactions cannot possibly account for such large effects, being several hundred times too small for this. It is one of the characteristic results of the new quantum theory that one of the manifestations of the electrostatic interaction between two electrons can be an energy term that is strongly dependent on the orientations of their spins, and yet is of the order of magnitude of the Coulomb interactions between the electrons.

We shall first treat the simple case of two hydrogen-like atoms, each with one valency electron which is acted upon by a pure Coulomb field, and we suppose that the nuclei are held at a fixed distance apart, $r_{a,b}$. In the absence of spin effects the Schrödinger equation for the two electrons would be

$$\left\{\frac{h^2}{8\pi^2 m}(\nabla_1^2+\nabla_2^2)+E+\epsilon^2\left(\frac{1}{r_{a,1}}+\frac{1}{r_{b,1}}+\frac{1}{r_{a,2}}+\frac{1}{r_{b,2}}-\frac{1}{r_{1,2}}\right)\right\}\Psi=0 \quad (1)$$

where 1 and 2 refer to the two electrons, a and b to the two nuclei and

$r_{a,1}$, $r_{1,2}$, etc., represent mutual distances. From the theory of the hydrogen atom we know the solutions of the equation

$$\left(\frac{h^2}{8\pi^2 m}\nabla_1^2+E+\frac{\epsilon^2}{r_{a,1}}\right)\psi_a(\mathbf{x}_1)=0 \qquad (2)$$

where $\mathbf{x}_1$ specifies the co-ordinates of electron 1, referred to nucleus a as origin. We also use an equivalent set of functions $\psi_b(\mathbf{x}_2)$ for the second electron. According to the elementary ideas relating wave functions with probabilities it might seem that the correct energy levels for the combined system would be obtained as follows. We write down, for the wave function of the combined system, the approximate wave function

$$\Psi=\psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2) \qquad (3)$$

whose square is a measure of the probability of finding electron 1 in the neighbourhood of point $(\mathbf{x}_1)$, and simultaneously electron 2 in the neighbourhood of point $(\mathbf{x}_2)$. Then (3) is an exact solution of (1) with the terms involving $r_{a,2}$, $r_{b,1}$, and $r_{1,2}$ deleted. To allow for the effect of these terms on the energy-levels we write

$$E=E_a+E_b+\int\int\left(\frac{1}{r_{a,2}}+\frac{1}{r_{b,1}}-\frac{1}{r_{1,2}}\right)|\Psi^2|d\tau_1 d\tau_2 \qquad (4)$$

that is, we take the extra, or perturbing, terms in the energy and consider, in turn, all possible configurations of the two electrons in space. Each such configuration has a certain probability, proportional to Ψ^2, of being realised, so that equation (4) amounts to saying that we take each possible configuration, multiply together the value of the perturbing energy and the probability of its being realised, and integrate over all possible positions of the two electrons. If we suppose that the wave functions ψ_a and ψ_b are normalised, so that when the absolute square of each, integrated over all space, is unity, $|\Psi^2|d\tau_1 d\tau_2$ is then equal, and not merely proportional, to the probability of finding electron 1 in the volume element $d\tau_1$ and, at the same time, electron 2 in the volume element $d\tau_2$. Naturally (4) is not *quite* correct, because the wave function is itself affected by the extra terms, and an improved result could be obtained by inserting an improved wave function into (4), the various successive approximations associated with alternate improvements of the wave function and the energy constituting perturbation theory. In the actual ferromagnetic problem it has not, so far, been possible to proceed beyond approximations similar to (4), which we have chosen to derive on a "commonsense" argument based on the relationship of a wave function and probability. The reader who desires a more accurate derivation is referred to standard treatises on quantum mechanics, but the "common-sense" argument throws rather more light on the physical meaning of an equation such as (4).

At this point we interpose a remark that we shall refer to again later (pp. 180–3). From our "elementary" derivation of (4) it is evident that we should get a better final result for the energy if, instead of using (3), we had started with a closer approximation to the final wave function. This we could do if, for example, we possessed the wave functions for an electron moving in the Coulomb fields of *both* nuclei (the "two-centre" problem). *Then* the only "perturbing" term would be $-\epsilon^2/r_{1,2}$, the effect of which on the energy would be allowed for, in a manner exactly analogous to (4), the total energy being that corresponding to the unperturbed wave function, together with an integral which, this time, only involves the *one* perturbing term. In the problem of the hydrogen molecule one probably gets just as good a final result by beginning with "hydrogen atom" wave functions as one would if one began with two-centre wave functions, because it is practicable to carry out perturbation calculations beyond the first approximation. A slightly increased error in the first approximation is then not a serious matter. However, it does not follow that a similar remark will hold if we are discussing more complicated molecules.

Before going further we must notice that wave functions such as (3) cannot always be used in practice, even as initial approximations. This brings us to the really characteristic feature of the new quantum theory, namely that it *must be so formulated that its observable predictions are not changed by the interchange of the co-ordinates of two identical particles such as electrons*. Now the predictions of quantum theory depend, not on a wave function itself, but only on its absolute square, so that the only physically acceptable wave functions are those *whose absolute squares are invariant against interchanges of identical particles*. For, if they were not, we should have the result that such an interchange would alter some observable result, and therefore that the occurrence of an interchange is, in principle, capable of experimental detection. This would contradict the hypothesis that the two particles were identical. Wave functions such as (3) will, therefore, only be physically acceptable if the functions ψ_a, ψ_b refer to the *same* quantum state, say the hydrogen-atom ground state. In other cases, we may not work with simple "product" wave functions, but wave functions to replace them, which at the same time satisfy both the wave equation, and the principle we have enunciated above, can be written down quite easily. These are

$$\psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2)\pm\psi_a(\mathbf{x}_2)\psi_b(\mathbf{x}_1) \qquad (5)$$

if ψ_a and ψ_b describe different quantum states, while we may continue to use functions of type (3) for particles in the same quantum state. The absolute squares of wave functions like (5) are unaffected by interchanging particles 1 and 2.

So far, our considerations have been based on the simple Schrödinger equation, which takes no account of electron spin. The rules for dealing with particles with spin have been built up semi-empirically, and the Dirac theory of the electron seems to be the only case in which the correct procedure for introducing the effect of spin into the wave equation is precisely known. We shall make the usual Pauli-Darwin assumption that a wave function can be *factored* into a "space part", which obeys Schrödinger's equation, and a "spin part", which consists of functions describing the orientation of the electrons relative to some fixed direction in space. One electron has only two such orientations, so its corresponding spin function can assume only two values. (This formalism has been shown to be practically equivalent to Dirac's exact treatment in the one-electron case, except for high electron velocities.) The "spin functions" for more than one electron are supposed to combine together in a manner quite analogous to the rules given by expressions (3) and (5) for possible functions. Thus, we have four possible types of spin function describing two particles. Classically, we should say that we had four possible cases, particles 1 and 2 may each have + and − spins, whereas quantum mechanically we must avoid statements equivalent to "Particle 1 has a + spin and particle 2 has a − spin", because we are not allowed to "label" identical particles.

By analogy with expressions (3) and (5), we set up possible spin functions as follows:

$\chi_+(1)\chi_+(2)$	Both particles+spin	(6a)
$\chi_-(1)\chi_-(2)$	Both particles−spin	(6b)
$\chi_+(1)\chi_-(2)+\chi_-(1)\chi_+(2)$	Opposite spins	(6c)
$\chi_+(1)\chi_-(2)-\chi_-(1)\chi_+(2)$	Opposite spins	(6d)

We postulate finally that, *to describe electrons, the only permissible wave functions are formed by multiplying together space functions of types* (3) *or* (5) *and spin functions of type* (6), *only those possibilities being retained that, as a result of a simple interchange of particles* 1 *and* 2, *lead to a reversal of sign of the whole wave function.* These postulates seem completely arbitrary and strange, but, in reality, the derivation of expressions such as (5) and (6) represents only a systematic "follow-up" of the consequences of the "identity principle" laid down above (p. 176). We refer to standard works on quantum mechanics for a discussion of a large number of other experiments that have been successfully interpreted on the basis of these postulates, but which were unintelligible on the basis of the old quantum theory. (Among such experiments we may mention the existence of "non-combining series" in the helium spectrum, the alternation of intensities of lines in band spectra, and the

existence of ortho- and para-hydrogen, and the anomalous scattering of α-particles by helium atoms.)

The final postulate has the consequence that *no two electrons may be in the same quantum level and have parallel spins*, which is Pauli's exclusion principle. The only two ways in which a change of sign of the complete wave function on interchange of two electrons can occur are through the appearance of spin function (6d), all three other spin functions keeping their signs unchanged, or through the appearance of a negative sign in expression (5), which is only possible if ψ_a, ψ_b refer to different energy-levels. That is, two electrons may be described by various types of wave function:

$$\psi_a(\mathbf{x}_1)\psi_a(\mathbf{x}_2) \times \text{spin function (6d)} \tag{7}$$

$$(\psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2)+\psi_a(\mathbf{x}_2)\psi_b(\mathbf{x}_1)) \times \text{spin function (6d)} \tag{8}$$

$$(\psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2)-\psi_a(\mathbf{x}_2)\psi_b(\mathbf{x}_1)) \times \text{spin functions (6a), (6b) or (6c)} \tag{9}$$

To allow for the possible effect of Coulomb interactions on the energies, functions such as (7), (8) or (9) must now be inserted into formula (4) (the wave functions being normalised before this is done). It can now be understood that the result of the perturbation calculation will give different results for the expected effect of the Coulomb interaction. The result will depend on just *which* type of wave function (7), (8) or (9), we insert into (4). Thus, we have found that the simple concept of *multiplication of probabilities*, which is implied by expression (3), and which is still correct for two or more *distinguishable* particles, cannot be accepted for identical particles, because *it omits to allow for the possibility that two such particles may change places between one observation and the next*. By systematically following up this idea, we have found out how to re-formulate the connection between wave functions and probabilities. For particles with spin, the spin orientation provides a possible "label" by which two otherwise identical particles could be distinguished, so that it is evident that the spin directions must be taken account of as well as the co-ordinates of the particles. The way to do this cannot be determined *uniquely* from first principles, but there is, as we have pointed out, a considerable body of experimental evidence that the use of wave functions such as (7), (8) and (9) is the correct process, or is, at least, a satisfactory first approximation, for two electrons.

We shall now look a little more closely at the correlation between the effect of the extra interaction terms and the spin orientations. We first of all notice that, if we are looking for the ground level of lowest energy of our combined system, it is natural to begin with a space function such as (3) that corresponds to two separate electrons each in their ground levels. If we do this, ψ_a, the ground-level wave function of $\mathbf{x}_1$ is multiplied by the same function of $\mathbf{x}_2$, and the only possible type of

spin function that can be associated with it is (6d). Now (6d) implies that the two spins are oppositely oriented. The second point is that, if we wish to find instead a level which can be associated with spin functions (6a), (6b) or (6c), we must arrive at a combined wave function like (9), which vanishes identically unless ψ_a and ψ_b represent *different* functions. If we are looking for levels of low energy, the best we can do is to let one of these functions correspond to the ground level of one electron, while the second corresponds to the first excited level. Thus, if we are looking for the level of lowest energy for which the two spins are parallel (described by functions (6a) or (6b)), *we are forced to start with initial wave functions of a somewhat higher energy than if we permit the spins to be antiparallel.* This remark is quite general, and applies, for example, whether we begin our perturbation theory with "hydrogen-atom" type wave functions or whether we used "two-centre" wave functions (i.e. those appropriate to the ionised hydrogen molecule). This means that there is, according to quantum mechanics, a decided *bias* in favour of a ground level for two electrons corresponding to *antiparallel* spins, but inspection of expressions (7) and (9) shows that this situation could conceivably be reversed, because of the extra contribution to the energy due to the perturbation terms in (4). The sign of this effect cannot be predicted *a priori*, but it can at least be said that, even if it is of the right sign, it cannot be appreciable unless there is some "region of overlap", i.e. some region of space in which both functions $\psi_a(\mathbf{x}_1)$ and $\psi_b(\mathbf{x}_2)$ are appreciable. This means that, if we are looking for conditions in which parallel spins are favoured, the nuclei have to be taken reasonably close together. However, it will not do to take them *too* close, since we know from spectroscopic evidence on helium and calcium, and other elements with two electrons in their outermost orbit, that the lowest "triplet" level, corresponding to wave functions like (9), lies well *above* the "singlet" ground level, corresponding to a wave function like (7). ((7) is a "singlet", because it can only be associated with *one* spin function (6d), (9) is a triplet, because there are three possible spin-functions (6a), (6b) or (6c), which would have slightly different energies in a magnetic field.) At this point we should mention a detail that sometimes causes misunderstanding. A spin function such as (6c) corresponds to the spins being *opposite*, yet it will lead to practically the same energy as (6a) or (6b), which correspond to the spins being parallel, because it is associated with the same types of space function. Thus the statement "Two electrons are in a triplet state" is not *quite* equivalent to saying "Two electrons have parallel spins". Also the statement "Two electrons are in a singlet state" implies that the spins *are* antiparallel, but the converse is *not* true. (Statements about the correlation between the perturbation terms and spin directions must be carefully worded with this point in mind.

Some books on quantum theory make formally correct statements, but omit to mention this rather subtle point explicitly!)

For the hydrogen molecule itself, there is *no* value of $r_{a,b}$, the distance between the nuclei, for which the symmetrical spin function gives the lowest energy (in fact the antisymmetrical spin function (6d) is the only one that corresponds to a *bound* state at all). All of this fits in nicely with the observed fact that ferromagnetism is comparatively rare. We have just given rough arguments that suggest that the effect cannot be expected at large internuclear distances because the perturbation integrals are numerically too small, nor at very small internuclear distances, for which the valency electrons would be exposed to a field not differing greatly from that of a single centre of force, resulting in a problem like that of the helium atom. Various workers have attempted to make this type of argument more precise, in order to correlate the various situations in which ferromagnetism occurs, in terms of the numbers of valency electrons, distance apart of the atoms, numbers of nearest neighbours, etc. It seems clear experimentally that the occurrence of ferromagnetism is the result of a delicate balance of several factors, for example the γ-modification of iron is *not* ferromagnetic although it can be obtained in a metastable state at temperatures well below the Curie point of ordinary iron and does not differ greatly from it in structure. Again, manganese is not ferromagnetic, but can be made so by alloying it with metals that do not destroy its lattice structure, but which do modify the "effective" numbers of valency electrons. The study of the interaction of hydrogen atoms that we have just outlined is usually known as the Heitler-London theory. The situation that we foreshadowed earlier has been confirmed in practice, namely that it makes little or no difference to the final results whether we begin with "hydrogen atom" or "ionised hydrogen molecule" type wave functions as the initial approximation. Nevertheless, points already arise, which, although they are readily attended to in the two-electron problem, do raise grave doubts about what may be the correct approach in a multi-electron problem.

A very simple example of such a difficulty occurs when we attempt to normalise a function such as (8) or (9). Consider, for example the three-electron problem, and suppose that we are working with a function antisymmetrical in the co-ordinates. It can be represented by a determinant

$$\Psi = \begin{vmatrix} \psi_a(\mathbf{x}_1) & \psi_b(\mathbf{x}_1) & \psi_c(\mathbf{x}_1) \\ \psi_a(\mathbf{x}_2) & \psi_b(\mathbf{x}_2) & \psi_c(\mathbf{x}_2) \\ \psi_a(\mathbf{x}_3) & \psi_b(\mathbf{x}_3) & \psi_c(\mathbf{x}_3) \end{vmatrix}$$

Expanding this determinant, squaring and integrating over the co-ordinates of electron 1, we find

$$\begin{vmatrix}\psi_b(\mathbf{x}_2) & \psi_c(\mathbf{x}_2)\\ \psi_b(\mathbf{x}_3) & \psi_c(\mathbf{x}_3)\end{vmatrix}^2 \times \int \psi_a^2(\mathbf{x}_1)\mathrm{d}\tau_1 + \text{two similar terms} \qquad (10)$$

$$-2\int \psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_1)\mathrm{d}\tau_1 \times \begin{vmatrix}\psi_b(\mathbf{x}_2) & \psi_c(\mathbf{x}_2)\\ \psi_b(\mathbf{x}_3) & \psi_c(\mathbf{x}_3)\end{vmatrix} \times \begin{vmatrix}\psi_a(\mathbf{x}_2) & \psi_c(\mathbf{x}_2)\\ \psi_a(\mathbf{x}_3) & \psi_c(\mathbf{x}_3)\end{vmatrix} + \text{two similar terms} \qquad (11)$$

Now if $\psi_a(\mathbf{x}_1)$, $\psi_b(\mathbf{x}_1)$ are hydrogen-atom-type solutions, they are "not quite" orthogonal, that is, if the nuclei a and b are a reasonable distance apart, ψ_b will be small everywhere near nucleus a where ψ_a is large and vice versa so the cross-terms will be small in any case. (In a problem with a reasonably small number of electrons, they can be explicitly evaluated if necessary.) If, instead, we worked with wave functions that were the *true* solutions of the problem of a single electron moving in the field of three nuclei, then the terms (11) would vanish *identically* (on account of the orthogonality of two *distinct* solutions of the generalised wave equation). Since expression (10) only contains squares of determinants, we can, without difficulty, integrate over the co-ordinates of a second electron, the cross-terms again vanishing because of the orthogonality. In the *many-electron problem*, the difficulty caused by using non-orthogonal wave functions as initial approximations can become extremely serious. Not only is there a "catastrophe", in that the number of cross-terms increases very rapidly with N, the number of electrons, but it may not always be correct to treat an individual term in (11) as small. Our discussion of the hydrogen-molecule problem has shown that the "exchange effect" (the difference in the perturbation terms that arises from substituting different types of wave function like (7), (8) and (9) into (4)) cannot possibly be large enough to offset the "bias" we have already referred to, in favour of function (6d) (anti-parallel spins), unless two atoms are reasonably close together. For, if terms like $\epsilon^2/r_{1,2}$ are to be large enough to overcome this bias, it means that their mean value must be at least of the order of the difference between the energies of the ground state and the first excited state, and this calls for the "mean" value of $r_{1,2}$ (actually a sort of harmonic mean is involved) to be comparable with the critical orbital radius. But it is in just these circumstances that the "overlap" terms of the type (11) begin to become significant also.

The existence of this "non-orthogonality catastrophe" in the many-electron problem seems to have been first pointed out by Inglis (1934) and the objection has been partially answered by van Vleck (1936). We shall return later on to this difficulty, but we now discuss some of the attempts that have been made to extend the theory to cover the many-electron problem. The extension had to be made in three distinct directions and, although progress has been made in all three, it is, perhaps, not surprising that the present situation is one of considerable

confusion. We clearly have to make some attempt to take account of the following further facts, after recognising that the discussion of the hydrogen-like atom has given us some very important clues:

(a) We have to devise some means of allowing for the fact that actual ferromagnetic atoms have more than one "valency electron" (however we define this term), and that more than one "electron shell" may be involved (however we define *this* term).

(b) We have to take account of the fact that these electrons can migrate through the lattice.

7.3. Extension to Atoms with many Electrons

As usual, we must simplify the problem by ignoring the effect of complete electronic shells, corresponding to filled bands in the metal. The treatment given in the last section can, in principle, be extended without difficulty to an assembly containing any number of electrons, by systematically enumerating all the space wave functions of types corresponding to (3) and (5) that satisfy the identity principle, and combining them with all permissible types of spin function. By the use of group theory Dirac in his *Quantum Mechanics*, Chap. 9, showed that the general result for the first-order perturbation could be written down in an extremely simple form, namely

$$E=-\tfrac{1}{2}\sum_{k,l}\mathcal{J}_{k,l}(1+4\sigma_k.\sigma_l) \qquad (12)$$

where σ_k and σ_l are the Dirac spin matrices for the kth and lth electrons, and $\mathcal{J}_{k,l}$ represent "exchange integrals" calculated in the manner we have already outlined above. Since this formula simply represents the generalisation of the "one-electron per atom" type of treatment outlined above, it must be subject to the same limitations of accuracy that may result from starting a calculation with a non-orthogonal set of initial space functions. For a further discussion of this question of non-orthogonality, the reader is referred to the review article by Slater (1953) where other references are given. Slater's constructive proposal is to use, as the starting point in a perturbation calculation, orthogonal sets of wave functions *describing the motion of one electron in a specific lattice*. In the treatment of the hydrogen molecule we saw that we might expect to get better results if we began with "two-centre" space functions rather than "hydrogen-atom" ones, both because the former are orthogonal and the latter are not, and also because they are better initial approximations. Whether it is practicable to carry out perturbation calculations to allow for Coulomb interactions using, for example, Bloch-type wave functions remains to be seen. Unless it proves possible to choose initial wave functions that are sufficiently close to the true ones, a first-order perturbation calculation involving a very large

number of electrons is likely to "blow up" completely, as occurred, for example in Heisenberg's attempt (1947) to take Coulomb interactions in the free-electron gas into account (p. 264). For the present, we shall make the customary assumption that an expression such as (10) is at least approximately correct, and we shall describe some of the theories that can be based on this idea. The interaction terms (10) superficially resemble magnetic interaction, but the exchange terms are, as we have pointed out, very much larger than those arising from true magnetic interaction. We have already discussed at length (Chapter VI) the consequences of the Weiss type of theory, in which these interactions are represented by an "effective field". Heisenberg made various attempts to generalise this theory to a many-electron atom, for a critical discussion of which the reader is referred to Fowler, *Statistical Mechanics*, van Vleck, *Electron and Magnetic Susceptibilities*, and to a very recent paper by Tredgold (1953). Heisenberg's guess, for a many-electron atom, was that the total effect of all the pair-wise interactions of type (12) between the electrons in the neighbouring atoms can be described by a Gaussian spread of possible energy-levels. This, at first, looked promising, as it seemed to lead to the prediction that ferromagnetism was theoretically impossible unless the number of nearest neighbours exceeded six (the actual condition for z nearest neighbours and y "active" electrons per atom being $y(y+2)z \geqslant 24$), but, as it also led to the prediction of a *lower* Curie temperature (a result of the low-energy "tail" of the postulated Gaussian spread "taking charge" at low enough temperatures), it seems that it is no real improvement on a theory of Weiss type.

We have also discussed at length the consequences of assuming that the interactions are effectively restricted to those between nearest neighbours. The many attempts at quantitative treatments of this assumption have nearly all been based on the Ising model, that is we restrict ourselves to the case of one magnetic electron per atom ($\mathcal{J}=\frac{1}{2}$), and suppose that each one may take up one of only two directions in space. Thus, the magnetic moments of any two atoms may be either parallel or antiparallel, and *no* other configurations are recognised. Expression (12) is rather more flexible than this, even for $\mathcal{J}=\frac{1}{2}$. Dirac's expression $\sigma_k.\sigma_l$ is to be interpreted in the same way as a scalar product of two vectors, so that all mutual orientations of two neighbouring spins are permitted, but the energy and probability of each orientation have to be described by means of Dirac's spin matrices rather than by classical vectors. P. R. Weiss (1948) has attempted to treat this type of interaction directly, by means of a modification of Bethe's method (1935), and was able to obtain definite results above the Curie temperature, to locate it (in cases where it exists), and to estimate the specific heat discontinuity.

7.3.1. Bloch's Theory of Spin-waves

Another attempt at an alternative treatment is due to Bloch (1930), who attempted to develop the consequences of an interaction of type (12) in a form that should be suitable at very low temperatures. Near absolute zero we should have nearly complete spontaneous magnetisation but, at any instant, a few reversed magnetic moments would be present. Now, if this assembly of magnetic moments were completely isolated from the outside world, both total energy and total magnetic moment would be "constants of the motion" in the quantum-mechanical sense. The interactions of the spins with one another would mean that, in the course of time, each one of them would undergo a reversal or deviation of its orientation, although at any one instant, the total *number* of reversed spins would be very small. Bloch's (1930) proposal amounts to describing this state of affairs by introducing the idea of "waves of spin deviation", in analogy with the Debye theory of solids, in which the displacements of the atoms in a crystal lattice from their mean positions are described by means of *sound waves*, of various frequencies and wavelengths, travelling through the whole crystal. As is well known, the Debye picture breaks down when the oscillations of individual atoms reach an amplitude comparable with the lattice distance, when, as we say, the principle of superposition of sound waves is no longer accurate. Similarly, the Bloch picture ceases to have any strict meaning as soon as the "deviation waves" passing over one electron call, when added up, for more than a complete reversal of its spin at any instant.

In practice, the spin-system is not completely isolated, because the thermal oscillations of the crystal lattice result in changes in the mean distances between the atoms, and thus modify the interactions between the spins and provide a means by which they can give energy to, or receive it from, the crystal lattice. This interaction, usually known as "spin-lattice interaction" has been much studied experimentally and theoretically, but we shall not discuss it further here. For present purposes, it is sufficient that a reasonably fast mechanism of this kind does exist, so that it is permissible to think of the assembly of spins as being able to gain or lose thermal energy. In these circumstances it is sensible to think of the "assembly of spins" as connected to a reservoir at a fixed temperature. The development of the theory can now proceed in a way quite analogous to the proof that Debye's theory represents a satisfactory first approximation for almost any solid at low enough temperatures. See, for example, Fowler, *Statistical Mechanics*, 2nd Ed., Chap. IV, for an account of the development of the Debye theory on these lines, and *ibid.*, Chap. XII, for an outline of the Bloch theory.

The main steps in Bloch's theory (1930) may be summarised as

follows, the process of determining possible energy-levels being really a generalisation of the process that we explained above, in which we found a special type of correlation between the perturbing energy resulting from the interaction between each pair of electrons and the relative directions of their spins. We follow Bloch's own method, but it is also possible, if desired, to set up a theory based on Dirac's operator expression (12). (For such a treatment see Kramers and Heller (1934) or Kittel, *Solid State Physics*, Appendix J.) We begin with a set of wave functions, all supposed to be normalised and orthogonal, exact solutions of the wave equation for the case of N atoms arranged equidistantly in a ring, interactions being neglected to begin with. Such wave functions may be written down as follows: For brevity we specify explicitly only the spin-configuration, numbering the atoms from 1 to N, and mentioning the numbers of those atoms that have a reversed spin. Thus, a typical wave function describing r reversed spins will be, if $\psi(f_1, f_2, \ldots f_r)$ are wave functions neglecting interactions,

$$\sum_{f_r} a(f_1, f_2, \ldots f_r)\psi(f_1, f_2, f_3, \ldots f_r)$$

We now have to carry out two steps. We first use the quantum-mechanical secular equation to determine possible values for the a's and the corresponding corrections in the energy to allow for the Coulomb interaction between the electrons, considering only the effect of the interactions between nearest neighbours. We shall specify explicitly in the secular equation only that part of each matrix element that depends on the spin orientations. We are only trying to compute the effect of the changes of spin orientation on the partition function, the remaining terms can have no effect on the magnetic properties. Having determined possible forms for the a's and the corresponding corrections to the energy to allow for the interactions between electrons, we have to make sure that we are using only such wave functions that satisfy the "identity principle", so that the absolute squares of the final wave functions are invariant against permutations of the electrons. (These "identity requirements" can always be satisfied, and do not affect the computed energies. The reader is referred to the original paper for details.)

As usual, the secular equation can be written down in terms of the matrix elements between the original ψ's resulting from the interactions, and we find that the only non-vanishing types of matrix element are those for which:

(a) Both "initial" and "final" wave functions refer to the same *number* of reversed spins.

(b) No more than *one pair* of unlike spins is permuted in passing

from the "initial" to the "final" wave function. (Interchange of two *like* spins does not change the wave function.)

All other types of matrix element vanish identically.

Requirement (a) arises from the fact that our wave functions each correspond to a definite total angular momentum, a "constant of the motion" in the language of quantum mechanics. This cannot be changed by a purely Coulomb interaction, but only by an interaction that involves the spin directions explicitly, such as the true magnetic interaction, or the interaction between spins and crystal lattice. The former is numerically very small compared with the Coulomb interactions whose effect we are studying. We have already explained that the spin-lattice interaction is the channel by which the spin-system is maintained in equilibrium with the outside world at a definite temperature. Provided that it is sufficiently strong, its detailed effects need not be considered further. We shall eventually work with a *canonical* ensemble, the number of spins being fixed, though sharing of energy with a reservoir is allowed.

Requirement (b) is simply a consequence of the fact that the Coulomb interaction is between *pairs* of electrons only. A wave function containing f_3 has been supposed to be orthogonal to one for which f_3 is absent. An interaction like $V_{1,2}$ cannot be capable of giving a finite matrix element involving two such wave functions, though an interaction like $V_{2,3}$ could do so. If we imagine these steps carried out, the secular equation for determining the new wave functions and corresponding energies can be written, after we simplify the problem further by considering only interchanges between unlike spins that are nearest neighbours (interchanges between like spins do not change the wave function) and supposing that all the such "exchange" energies are equal to $\mathcal{J}$,

$$\eta a(f_1 \ldots f_r) = \mathcal{J} \sum_{f'} a\{(f_1 \ldots f_r) - a(f_1' \ldots f_r')\} \qquad (13)$$

where η represents a possible contribution to the energy of the whole assembly for a configuration containing r reversed spins, and the sets f' differ from f only by an interchange of one pair of unlike neighbouring spins. We use, as a trial solution of the set of difference equations (13), the following, of a type often used in problems associated with repeating lattices

$$\exp(i\kappa_1 f_1 + i\kappa_2 f_2 + \ldots + i\kappa_r f_r) \qquad (14)$$

We have to take linear combinations of functions such as (14) and others derived from them by permuting the κ's and f's, in order to satisfy boundary conditions (say of periodic type) as well as equations (13). The reader is referred to Bloch's original paper (1930) or to Fowler, *Statistical Mechanics*, Chap. XII, for a discussion of the detailed points involved.

The possible energy-levels for a ring of N atoms are given by

$$\eta_+ \approx 4\mathfrak{J} \sum_{\nu=1}^{r} \sin^2\left(\frac{\pi k_\nu}{N}\right) + \text{terms independent of spin functions} \quad (15)$$

where $\kappa_\nu = 2\pi k_\nu/N$ and the smaller k_ν's are nearly integers. (The imposition of periodic boundary conditions means that there are N possible k_ν's, any r of which are to be selected in forming expression (15).) For k_ν small, it is sufficiently accurate to replace the sine functions by their arguments (in just the way that is done in deriving Debye's theory of specific heats from a "lattice model". See Fowler, *Statistical Mechanics*, 2nd Ed., Chap. IV).

The fact that we have a finite number of k_ν's also has its analogue in crystal lattice theory; the discontinuous lattice structure imposes a "cut-off", in the sense that Debye spectra (or others that follow from more accurate versions of the Debye theory) all stop at wavelengths comparable with the interatomic distances. Expression (15) indicates a "cut-off" that occurs in a quite similar way, but, at low temperatures, we are only interested in small values of the k_ν's, so this point is not of great importance.

At this stage it is useful to discuss the physical meaning of "excitations" such as those described by expression (14). In quantum mechanics we only recognise two possible energy-levels of each individual spin in an external magnetic field, but this is not at all the same thing as saying that each neighbouring pair *must* be either parallel or antiparallel as is assumed in the Ising model. In fact, if we have just two electrons, we may add together a wave function (associated with a spin function stating that the spins are antiparallel) with another wave function associated with a parallel spin function. We can interpret this "mixed" wave function in various ways, but it is certainly quite in order to say that the relative amplitudes of the two types of spin function are a measure of the mean inclination of the two spin axes to one another, averaged over a period of time. Equally it is in order to say that the pair spends a fraction of its time in the parallel orientation and the remainder of its time in the antiparallel orientation. However, if we have a *line* of atoms, an excitation such as (14) of long "wavelength" describes a situation very similar to what we shall postulate later on (p. 209) as the probable state of affairs as we travel through a "domain" wall, namely a *gradual* change in the spin-orientation extending over many lattice distances. If we attempted to describe such a situation on the basis of an *Ising* model we should run into a serious difficulty, because, if *each* neighbouring pair of spins is extremely likely to be parallel, the few reversals that do occur in a line of spins would, at any instant, be distributed practically *at random* along the line, and there is nothing in this situation corresponding to the "wavelength" of a spin

excitation, the corresponding gradual change in orientation or the "effective thickness" of a domain wall.

Thus, the Bloch theory gives a natural description of these situations, that are quantum-mechanically quite possible but are hard to describe within the framework of a Heisenberg or Ising treatment. The latter types of theory are better suited to describing *abrupt* domain boundaries, but there is a very large body of evidence (see pp. 209–14) that such boundaries *are* of finite thickness. According to the Bloch theory we start at very low temperatures with a completely magnetised state, but, as we raise the temperature, the equilibrium state corresponds to greater and greater mean numbers of reversed spins, until the spontaneous magnetisation drops to zero. We shall now trace this process.

The generalisation of (15) to two or three dimensions offers no difficulties of principle, as long as we still neglect all exchange integrals except those between pairs of nearest neighbours. (Many of the complications of crystal lattice theory arise just because we *have* to take second-nearest-neighbour interactions into account, but, in the magnetic problem, there seems to be no imperative need for doing likewise.) We can then write, for the various possible energies due to exchange effects in the simple cubic lattice:

$$\eta_r = 4\mathcal{J}\sum_{\nu=1}^{r}\left[\sin^2\left(\frac{\pi k_\nu}{N^{1/3}}\right)+\sin^2\left(\frac{\pi l_\nu}{N^{1/3}}\right)+\sin^2\left(\frac{\pi m_\nu}{N^{1/3}}\right)\right] \qquad (16)$$

which we shall represent by the expression, valid at low energies which alone are relevant as $T\to 0$:

$$\eta_r = \frac{4\mathcal{J}\pi^2}{N^{2/3}}\sum_{\nu=1}^{r}(k_\nu^2+l_\nu^2+m_\nu^2) \qquad (17)$$

In an external magnetic field H, the energy associated with r reversed spins is $(2r-N)\mu H$, while the partition function called for by an expression (17) is identical with that referring to r fictitious "systems", each of which can "occupy" one of the "energy-levels" arrived at by choosing one of the possible k's, one of the possible l's, and one of the possible m's, squaring and adding. In the three-dimensional case, there will be $N^{1/3}$ lattice distances in each direction, and therefore $N^{1/3}$ possible choices of k_ν etc. The complete partition function is, therefore, given by

$$\log f \approx \frac{NH\mu}{kT}+\sum_{k_\nu,l_\nu,m_\nu=0}^{N^{1/3}}\log\left(1-e^{-\{2H\mu+(4\mathcal{J}\pi^2/N^{2/3})(k_\nu^2+l_\nu^2+m_\nu^2)\}/kT}\right) \qquad (18)$$

Expression (18) is, except for the factor $\exp(NH\mu/kT)$, formally identical with the partition function for a perfect gas whose molecules obey Bose statistics. The transcriptions that one would have to make to pass from one expression to the other are

$$e^{-2\mu H/kT} \rightarrow \lambda, \quad \frac{4\mathcal{J}\pi^2}{N^{2/3}} \rightarrow \frac{h^2}{8md^2}, \quad k_\nu, l_\nu, m_\nu \rightarrow p, q, r \tag{19}$$

(See also p. 303.) Bloch (1930) shows that expression (18) gives the correct behaviour as $T \rightarrow 0$, even though the number of possible complexions is apparently overestimated.

This formal analogy between the "reversed spins" in this problem and the gas molecules which occupy energy-levels in a cubical enclosure of side d given by

$$\epsilon_{p,q,r} = \frac{h^2}{8md^2}(p^2+q^2+r^2) \tag{20}$$

has been remarked upon by quite a number of people, though the way in which the energies are originally calculated is quite different, e.g. equation (16) has no analogue in the perfect-gas problem. The thermodynamic consequences of expression (20) and various possible generalisations of it are very well known because of the probable connection between such models and the liquid helium problem. (See p. 303.) If, in expression (18), we can replace the summations over k_ν, l_ν, m_ν by integrations, the validity of which step we shall consider in a moment, we find for the log (partition function) the expression

$$\log f \approx \frac{NH\mu}{kT} + \sum_{S=1}^{\infty} (\sqrt{\pi})^3 \left(\frac{N^{2/3}}{4\mathcal{J}\pi^2}\right)^{3/2} \frac{(kT)^{3/2} e^{-2SH\mu/kT}}{S^{5/2}} \tag{21}$$

by expanding (18) in ascending powers of the exponential, then integrating each term. This leads to an intensity of magnetisation

$$I = kT\frac{\partial(\log f)}{\partial H} = N\mu - \frac{N\mu}{4\pi^{3/2}}\left(\frac{kT}{\mathcal{J}}\right)^{3/2} \sum_S \frac{e^{-2SH\mu/kT}}{S^{3/2}} \tag{22}$$

which approaches a finite limit as $T \rightarrow 0$, so that the theory predicts spontaneous magnetisation which falls short of absolute saturation by a term varying as $T^{3/2}$. (The same form of result, with different numerical coefficients, is obtained for other three-dimensional lattices.)

For a two-dimensional square lattice, a distinctly different situation occurs, the expressions corresponding to (21) and (22) being:

$$\log f \approx \frac{NH\mu}{kT} + \sum_S (\sqrt{\pi})^2 \frac{N}{4\mathcal{J}\pi^2} \frac{kTe^{-2SH\mu/kT}}{S^2} \tag{23}$$

$$\begin{aligned} I &= N\mu\left(1 - \frac{kT}{\mathcal{J}}\frac{1}{2\pi}\sum_S \frac{e^{-2SH\mu/kT}}{S}\right) \\ &= N\mu\left(1 + \frac{kT}{2\pi\mathcal{J}}\log\left(1-e^{-2\mu H/kT}\right)\right) \end{aligned} \tag{24}$$

the summation of the series in (24) now being possible in finite terms. In this case, we cannot proceed to the limit $H \rightarrow 0$ without the whole

theory becoming invalid. The number of reversed spins of course cannot exceed N, and it cannot approach $N/2$ without several of the approximations that we have had to make in the course of the work becoming poor, indeed the whole picture of "spin excitations" moving about the lattice independently of one another then seems to be invalid. Expression (24) would, however, remain valid as long as the applied field H was maintained at *any* finite value, however small, in which case it *always* predicts a completely magnetised state as $T\rightarrow 0$. For any finite T, a finite H would, however, be required for expressions (23) and (24) to remain valid, the theory breaking down as soon as (24) calls for $I\approx 0$. With a completely isotropic model it is entirely reasonable that a small field should have to be retained in order to give the spins a "preferred direction" in which they can point. If we maintain H at a fixed positive value and let T grow from zero we find that Nernst's theorem is completely satisfied, at $T=0$ not only $\partial I/\partial T$ but all higher derivatives of I with respect to T also vanishing ($T=0$ being a "stop-point"). If, however, we let T diminish from a finite value ($\gg H\mu/k$), keeping H constant, the theory still predicts saturation as $T\rightarrow 0$, but the departure from saturation is now apparently proportional to $T\log T$, i.e. Nernst's theorem, which requires $\partial I/\partial T$ to approach zero as $T\rightarrow 0$, is *apparently* violated, and we have to reach a temperature *below* $H\mu/k$ before we get behaviour in conformity with Nernst's theorem. A similar point is made by Klein and Smith (1951) in their discussion of the ferromagnetism of thin films. This behaviour can be contrasted on the one hand with that of the Ising or Weiss-Heisenberg theories, in both of which only two directions are allowed to the magnets, and the departure of I from saturation is along a curve of the type $\exp(-T/T_0)$ and on the other hand with that of the original Langevin-Weiss model, which has a singularity in the entropy at $T=0$, and for which the departure of I from saturation is a *linear* function of T. Although Langevin's model (like Bloch's) is completely isotropic, the application of a small magnetic field to "tell the magnets in what direction to point" does *not* enable *this* model to obey the Nernst theorem, the singularity in the entropy persisting, because the number of possible configurations of N magnets is infinite in the classical case.

It seems that Bloch's statement in his original paper (1930) that his two-dimensional model is *not* ferromagnetic is fundamentally incorrect, the mistake having arisen through applying the limiting process $H\rightarrow 0$ *too soon*, thereby causing the theory to "blow up". The only physically correct way of looking for "ferromagnetism at absolute zero" corresponds to the limiting process $T\rightarrow 0$ with $H=0^+$. Unfortunately, the statement has been copied by nearly all subsequent writers. It can, however, be said that the spontaneous magnetisation is much more likely to be disturbed by thermal agitation in the two-dimensional

Bloch model than in the three-dimensional one, and that the Ising and Weiss-Heisenberg models are still more "resistant" to thermal agitation.

One fundamental reason for this difference is the isotropy of the Bloch model without a field, and a second reason has been given by Herring and Kittel (1951); it is simply that the energy required to pass from the spontaneously magnetised ground state to a completely unmagnetised state is much smaller for the Bloch model. In an $N \times N$ lattice, we require, on the Ising model, an energy of at least $N\mathcal{J}$ (where $\mathcal{J}$ is the exchange integral), since N is the smallest possible length of a boundary between + and − spins, in order to get a state with zero magnetisation. On the Bloch model we can have a *gradual* boundary, just like a domain wall (p. 209). As we move through such a boundary, we may have each spin inclined to its neighbours at an angle $\approx \pi/N$, and the total interaction energy, of such a demagnetised state, that of the completely magnetised state being taken as zero, is $N^2\mathcal{J}\{1-\cos(\pi/N)\}$ $\approx \pi^2\mathcal{J}/2$ since there are N^2 pairs of nearest neighbours. The appearance of demagnetised states as a result of thermal agitation is therefore much more likely on the basis of the Bloch model than it is on the Ising model, hence the different behaviour of I as a function of T as $T \to 0$.

A further point that needs a brief discussion is the validity of replacing sums by integrals in evaluating expressions (21) to (24). In the theory of the Bose-Einstein gas it is well known that, at very low temperatures, this replacement leads to absurd results, and that it is necessary to add in separately the term in the log (partition function) corresponding to $p=q=r=1$, that is the term corresponding to the very lowest level given by (20). [The necessity of such a correcting term is an elementary consequence of the Euler-Maclaurin sum formula. See p. 303.] One might reasonably ask if similar corrections ought not to be made in expressions (21)–(24) for the same reason. This point has been raised by Kubo (1953) and by Klein and Smith (1951) who give arguments in favour of omitting the term corresponding to $k_\nu = l_\nu = m_\nu = 0$. It seems clear, however, that the term is of no *practical* importance (although it *appears* to diverge as $H \to 0$, and thus seems to spoil the theory completely). Physically, it corresponds to simultaneous rotations of *all* the spins, which would *not* affect the spontaneous magnetisation, but would affect the magnetic moment *measured in a fixed* direction. However, it does not seem as if the extra term, equal to

$$\frac{2\mu e^{-2H\mu/kT}}{1-e^{-2H\mu/kT}}$$

in equations (22) and (24), has any *practical* effect, because $\mu H/kT$ has only to be somewhat larger than $1/N$ for the effect of the extra term on the magnetisation to be negligible. Such a field is quite indistinguishable

from zero in a large assembly. The difference made by including the extra term is not important. It amounts to a change from "any field however small" to "any field $> kT/N\mu$" which become equivalent for large N.

If we compare these considerations with those of domain theory (p. 207) it is perhaps reasonable to say that the Ising or Heisenberg theories correspond to the case of very large anisotropy in domain theory, when we get *abrupt* domain boundaries of *high* energy content, while the Bloch theory corresponds to a completely isotropic model, when we get very *thick* domain "walls" of *small* energy content. As we approach the Curie point from below it is to be expected that, at very low temperatures, the Bloch theory should give the best description of the variation of spontaneous magnetisation with temperature, and this is borne out by comparisons that have been made with experiment. (See, for example, P. Weiss (1934), Fowler, *Statistical Mechanics*, 2nd Ed., p. 500.) On the other hand, it is clear that the approximations that have had to be made must break down almost completely as we approach the Curie point, and that here the theory can do no more than predict orders of magnitude correctly. In a situation of this kind, the "range of validity" of a theory is partly a matter of definition and partly of opinion. The suggestion that the theory has no *practical* range of validity at all has been made by Wohlfarth (1949) and answered by Herring and Kittel (1951). The main source of trouble would seem to be that the model apparently predicts close encounters of "reversed" spins, which admittedly correspond to no physical feature (see p. 184), but the statistical probability of such a fictitious event should be comparable with that of two nearest neighbour spins being reversed which is small until the spontaneous magnetisation drops to about 90–95 per cent of absolute saturation. This occurs at a temperature of about one-half to one-third the Curie temperature. The calculations of Holstein and Primakoff (1940) suggest that the "spin-wave theory" should give only small errors below this, and this conclusion seems to be entirely borne out by the comparisons with experiment, departure from the $T^{3/2}$ law becoming noticeable at just about the temperatures that, on this basis, we should expect the theory to break down.

Very recently, a fresh examination of the problem by Schafroth (1954) shows that a proper development of the consequences of Bloch's model in the form of an ascending series in T would converge extremely slowly (if at all) in the neighbourhood of the Curie point, even if the model itself is considered acceptable in that region.

7.3.2. Stoner's Picture of "Electron Bands"

A picture that differs from both Heisenberg's (1928) and Bloch's (1930) is due to Stoner (1938; 1939). According to this, one begins with

the idea that the electrons are satisfactorily represented by wave functions of "band" type, that is, we regard them as completely free to move through the crystal. If we began, say, with a distribution of energy-levels according to the "$E^{1/2}$" law characteristic of "electrons in a box" (or in a periodic lattice potential of small amplitude), it is easy to make a calculation of the susceptibility, the so-called "spin paramagnetism", which occurs simply because, in a magnetic field, energy considerations favour the lining up of the spins. If, however, we have a pair of electrons in a doubly occupied level, one of the electrons will have to find an unoccupied level of slightly higher energy in order to contribute to the magnetisation, because two spins in the *same* level cannot "line up". This means that the energy gained by one of the spins from the magnetic field has to be balanced against the loss of energy from its having to transfer to a higher level, and, for any assumed band structure, a calculation of the expected paramagnetic susceptibility can be made. In practice, it is small because only those electrons near the critical Fermi energy will contribute appreciably. (Well above the Fermi energy, there are very few electrons, well below it there are plenty of electrons but very few nearly vacant levels.) We have the following expression for I, the intensity of magnetisation,

$$I = kT\frac{\partial(\log f)}{\partial H} = kT\frac{\partial}{\partial H}\sum_r \log\left(1+\lambda e^{-(\epsilon_r \pm \mu H)/kT}\right) \qquad (25)$$

where we have to use Fermi statistics rather than Boltzmann statistics to allow for the fact that the electrons are now not bound to a lattice point, but are free to move through the metal.

Stoner now assumes, *ad hoc*, that the energy of the whole assembly has to be corrected by a term proportional to I^2, whose origin is attributed to an exchange effect of the same general type as that discussed by Heisenberg (1928). We have already mentioned the difficulties that arise on attempting to apply perturbation theory to a many-electron assembly (p. 180) and we shall not discuss them again. Wohlfarth (1953) gives a review of various attempts that have been made to estimate this exchange term *a priori*, but such calculations prove extremely difficult. The consequences of the exchange term are very similar to those of the simple Weiss theory, in fact the Stoner theory reduces to a Weiss model in the limiting case when the electrons have a very *low* degeneracy temperature. The free energy can be deduced from the partition function in the usual way, and the interactions allowed for by introducing the term $\frac{1}{2}\alpha I^2$ into the energy. As with the Weiss model, we can show that this is equivalent to replacing H by an effective field $H+\alpha I$. That is, each energy level is now a function of I and thus of the temperature. This sort of situation has already been considered (p. 123).

$$\log f = \sum_r \log \{1+\lambda \exp [(-\epsilon_r+\mu H+\mu\alpha I)/kT]\} + \sum_r \log \{1+\lambda \exp [(-\epsilon_r-\mu H-\mu\alpha I)/kT]\} \quad (26)$$

As in the Weiss theory we have to solve an implicit equation, but here the equation involves an integral of Fermi-Dirac type, and considerable numerical work is required to get the spontaneous magnetisation and susceptibility curves for various ratios of the strength of the interaction to the degeneracy temperature. Assuming an "$E^{1/2}$"-type band we find where a is a constant,

$$\log f = \int_0^\infty a\epsilon^{1/2} d\epsilon \begin{bmatrix} \log \{1+\lambda \exp (-\epsilon+\mu H+\mu\alpha I)/kT\} + \\ \log \{1+\lambda \exp (-\epsilon-\mu H-\mu\alpha I)/kT\} \end{bmatrix} \quad (27)$$

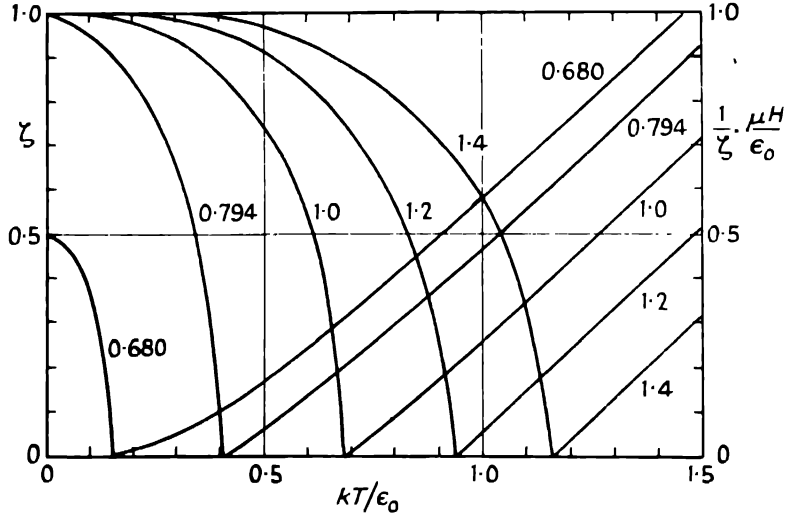

Fig. 27. Spontaneous magnetisation below and inverse of susceptibility above the Curie point as functions of kT/ϵ_0. ζ, relative magnetisation. The numbers on the curves give the values of $k\theta'/\epsilon_0$. The two curves on the left correspond to $k\theta'/\epsilon_0$ values giving $\zeta_0=0{\cdot}5$ ($k\theta'/\epsilon_0=0{\cdot}680410$) and the critical value for complete saturation at absolute zero, $\zeta_0=1{\cdot}0$ ($k\theta'/\epsilon_0=0{\cdot}793701$). The falling curves (scale on left) give the spontaneous magnetisation below the Curie point, the rising curves (scale on right) a quantity proportional to the inverse of the susceptibility ($\chi \propto \zeta/H$). (*After Stoner.*)

Wohlfarth (1951) was able to get simpler results by assuming a *rectangular* structure for the conduction band [$N(\epsilon)$ independent of ϵ], and, comparing them with the numerical results following from the "$E^{1/2}$"-type band, was able to show that band shape did not affect the results qualitatively. Various interesting effects *do* occur as the ratio of ϵ_0, the critical Fermi energy, to the magnitude of the interaction term $N\mu^2\alpha$ is changed. For example:

(a) At $\epsilon_0=0$, we have the Weiss theory, with the same spontaneous magnetisation curve and "Curie line". A set of "spontaneous magnetisation" curves for different values of $T_0=\epsilon_0/k$ is shown in fig. 27 and it will be seen that, for finite T_0, the Curie line, representing $1/\chi$ plotted against T, becomes curved, and a corresponding change occurs in the spontaneous magnetisation curves.

(b) If the ratio $N\mu^2\alpha/\epsilon_0$ falls below the critical value $2^{-1/3}$ the spontaneous magnetisation at absolute zero no longer corresponds to "full saturation" or "complete alignment". This arises for the reason just explained in connection with the susceptibility. Full saturation would require that each level be occupied only singly, so that we use up twice as many energy levels and raise the total energy by a factor of $2^{2/3}$, and the difference may not be fully compensated by the assumed interaction. The state of lowest energy in such a case will be one in

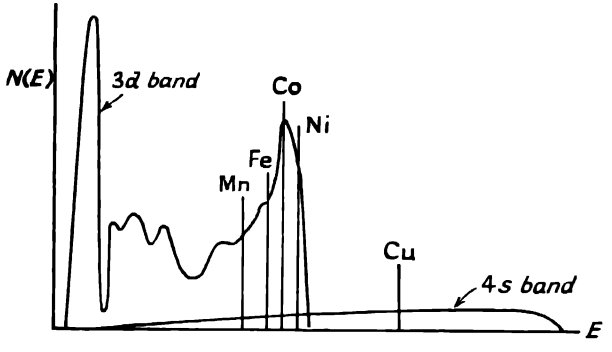

Fig. 28. Approximate form of 3*d* and 4*s* bands in transition metals, according to Krutter. Vertical lines indicate approximate Fermi energies for each metal.

which the lower levels are doubly occupied and contribute nothing to I, but the higher levels are singly occupied and do contribute. If the ratio $N\mu^2\alpha/\epsilon_0$ falls below 2/3, there is no ferromagnetism.

These features are qualitatively the same whatever the band shape may be. It would be possible to assume a band structure corresponding to what probably exists in an actual ferromagnetic case, for example, on Krutter's (1935) calculations of the probable form of the 3*d* and 4*s* bands (fig. 28), but the numerical evaluation of the resulting Fermi-Dirac integrals and the solution of the implicit equations would require an enormous amount of labour. Moreover, Wohlfarth's preliminary calculations (1953) indicate that a more correct interaction probably contains an appreciable contribution proportional to I^4 besides the term in I^2 assumed by Stoner. This would not change the results qualitatively, but can make a considerable difference to the detailed predictions. See Hunt (1953). Thus, once again, we are not yet in a position to make any

very significant *numerical* comparisons of theory with experiment. The following semi-quantitative points *are*, however, important.

(a) The theory provides one of many possible explanations of the observed curvature of the Curie line in the immediate neighbourhood of the Curie point. Others are listed on p. 201.

(b) The theory could, in principle, explain almost *any* reasonable variation of the spontaneous magnetisation with temperature by making a suitable assumption about band shape.

(c) Since the saturation at low temperatures *can* be incomplete, we get a neat explanation of the fact that the limiting magnetisation at low temperatures does *not* always correspond with the slope of the Curie line, although, on most of the other pictures, the "effective number" of electrons contributing to the magnetisation ought to be the same calculated by either method.

(d) It seems almost essential to take the band structure into account, both in order to link up with the ordinary theory of metals, and also in order to understand such results as the fact that the slope of the Curie line for Ni corresponds to about 0.6 "magnetically active" electrons per atom. Such a result is almost unintelligible if we think of the magnetically active electrons as bound to lattice points. On the other hand, it follows readily as a consequence of an "overlapping band" structure. As in ordinary conduction theory, if two bands overlap, the electrons, corresponding to those which in separated atoms occupy one shell, may be shared between two bands. The reader is referred to an ingenious attempt by van Vleck (1953) to compromise between these two extreme assumptions of "completely free" and "completely bound" electrons.

7.3.3. Zener's Discussion of Exchange Effects

Zener's (1951 a, b) contention is that ferromagnetism cannot be properly understood even qualitatively except on a "two-shell" model, that is, both the 3*d* and 4*s* levels of the electrons must be considered explicitly. It seems to be generally agreed that the electrons in 3*d* levels can be treated roughly as "localised" in the sense of "belonging" to one atom. It then seems that exchange effects *within* each atom result in these electrons "lining up" to the maximum extent permitted by the exclusion principle. This result is known as "Hund's rule", and was obtained originally on spectroscopic evidence. This seems in agreement with what is known about the paramagnetism of salts of the iron group and rare earths (see van Vleck, *Electric and Magnetic Susceptibilities*, pp. 241, 285). The point at issue is the mechanism by which the *total* magnetic moments belonging to two or more such atoms are aligned. We have already discussed the idea that this can be explained if we

postulate a mechanism similar to the interaction between "hydrogen-like" atoms. This, as we have seen, inevitably leads to "antiferromagnetic" coupling at both large and small separations of two atoms, but a "ferromagnetic" coupling is, in principle, quite possible over a small range of separations, though no very clear statement of the properties that a wave function must have in order to give rise to such a result ever seems to have been given. (It certainly does not occur with two hydrogen atoms, but the possibility remains open if there is more than one electron per atom.)

Zener's proposal is to discard this assumption as artificial, and to suppose that, as for hydrogen atoms, the *direct* interaction between two 3*d* shells is antiferromagnetic at *all* distances. He then considers the electrons in the 4*s* bands as being the "conduction" electrons, supposes that they can be represented properly by a "band" picture, and suggests that the 3*d* shells of neighbouring atoms are aligned by the indirect effect of their exchange interactions with this conduction band, and it is *this* interaction that he proposes to assume to be ferromagnetic. On this basis, we should have, taking account of the exchange interactions between *d* shells, within the *s* band, and between the *s* band and the *d* shells the following very approximate expression for the spin energy,

$$E_{\text{spin}}=\tfrac{1}{2}\alpha S_d^2-\beta S_d S_c+\tfrac{1}{2}\gamma S_c^2 \qquad (28)$$

where α, β and γ are constants and S_d, S_c represent the mean component of spin per atom along the magnetisation direction associated respectively with the *d* shell and the conduction band. For a given S_d, expression (28) is a minimum for $\beta S_d=\gamma S_c$, and the resulting "effective interaction" between *d* shells would be ferromagnetic or antiferromagnetic according as $\beta^2>$ or $<\alpha\gamma$. If β is large enough, we get ferromagnetism, but if we bring two atoms very close together α becomes large also and the effective interaction becomes antiferromagnetic. For a very large lattice spacing ferromagnetism is unlikely, for reasons already explained (p. 179). Thus in this way it is also possible to understand why ferromagnetism is to be expected only for a *certain range* of atomic spacings, as the experimental facts suggest.

This picture is quite compatible with the Stoner picture (1938) where nothing very definite about the *origin* of the interaction is assumed; we only guess its approximate form and behaviour. The thermodynamic consequences of the model will be precisely the same whether the interaction occurs directly between the *d*-electrons, as is implied by the original Heisenberg picture, or indirectly by a mechanism like Zener's. Zener has brought forward some indirect experimental evidence in support of his hypothesis. The reader is referred to the review article by Zener and Heikes (1953) for a summary of this.

7.4. Discussion

One can, at present, do no more than report on the very intricate controversies on the fundamental mechanism of ferromagnetism that are at present in progress, and of which an outline has been given above. To the writer it seems almost certain that each of the theories so far mentioned contains a large measure of truth, and that what is now called for is an attempt to *synthesise* some of the differing points of view rather than to try and "decide between them" experimentally. Any complete synthesis is unlikely at present, and, even if it could be made on the quantum-mechanical side, it would probably lead to a statistical mechanical problem beyond the present resources of mathematics to work out with sufficient accuracy. However, it does seem that certain *partial* syntheses of some of the different points of view may soon be possible. As just one example, it ought to be possible to arrive at some compromise between the "spin-wave" picture, in which we treat the electrons as effectively *fixed*, and a "band" picture, in which the electrons are considered perfectly free to migrate through the lattice, "carrying their spins with them". One feels, though it is difficult to make the idea precise, that one ought to be able to find some compromise between the two very different ideas of "one-electron" energy-levels, and "spin-excitations", the latter not being defined unless we have quite a large number of electrons. We have met the same type of situation before in discussing the liquid state which is not properly described either by "one-particle" models nor by "Debye-like" excitations, and the difficulty is particularly acute for liquid helium, as we shall see later (p. 300). The corresponding problem is to find some means of bridging the gap between "gas-like" and "solid-like" models. These, as we know, behave quite differently at low temperatures, and the difference is not surprising in view of the great differences in the mathematical methods used. In a "gas-like model" we have infinitely many possible *modes* or energy-levels, but we limit *the total number of elementary systems or particles* in them by a "selector variable" or similar technique. In a "Debye-like model" we place no limits on the individual or total numbers of "excitations" (here sound quanta), but we do take account of the finite subdivision of matter by limiting the total number of *modes* by a "cut-off" or equivalent procedure. The formal correspondences between "sound-wave" and "spin-wave" are fairly evident on a comparison of the treatments, and the expression "electron-gas" is familiar enough to make it unnecessary to elaborate that correspondence further. (These correspondences cannot be pushed too far—we have suggested that the spin-wave treatment is analogous to the Debye treatment, but we have also noticed the close *formal* similarity between the final results of the "spin-wave" theory and that of the perfect *Bose* gas.)

The kernel of the present controversy on ferromagnetic theory seems to amount to an argument about the most promising way of taking account of the interactions between individual metal atoms in order to build up a satisfactory theory of a metal. This difficulty is already becoming serious even when we have a problem so simple as an alkali metal, an atom of which we can treat as a positive core plus a *single* valency electron. (Even the problem of the imperfect gas, specialised to the inert gas case with *no* valency electrons at all, is far from easy to handle quantum-mechanically.) It is, therefore, not surprising that serious difficulties of principle become apparent when we try to erect two further stories on an already shaky foundation, the separate atoms of the transition metals each containing *two incomplete shells*, each of which contains *more than one* electron. This really brings us back to the question of what exactly we ask for from a "theory". There seems no doubt at all that Heisenberg's (1928) idea on the explanation of ferromagnetism in terms of exchange effects originating from Coulomb forces is fundamentally correct, and it is also fairly evident that exchange effects will usually be antiferromagnetic, and that this situation can, in principle, be reversed at certain lattice spacings, for one or more out of a number of possible reasons. Are we to be content to leave matters in this state, perhaps for some time to come? In the ordinary theory of metals, we are not yet in a position to *predict* the expected crystal structure of a metal even if we have as preliminary data a good calculation of the wave functions of an individual atom. Once given this structure as a datum we can often progress a very long way in interpreting the properties of the metal.

The answers to such questions are, once more, matters of taste, but, before we attempt to answer this particular one, it seems advisable to remind ourselves that, as things stand at present, the experimental evidence that might help us to "decide" between various possibilities is decidedly scanty, a situation that is in strange contrast with the enormous amount of experimental work that has been done on ferromagnetics. This matter has already come up (p. 117), but it is perhaps helpful to review here the types of experiment that may, later on, help in "decisions" between some of the "rival" theories.

We have already referred to the difficulties and confusion caused by the frequently quoted comparison of the measurements of the variation of spontaneous magnetisation with temperature with the crude Weiss theory. Measurements of spontaneous magnetisation are scarce and difficult to carry out. A review of the reliable material, together with some new results on copper-nickel alloys, is given by Sucksmith *et al.* (1953). The intervention of domain effects prevents a direct measurement of spontaneous magnetisation in zero field, and we have to resort to indirect methods, such as measuring the magnetisation in a field

large enough to remove domain "walls", afterwards trying to correct for the small change in intrinsic magnetisation that would result if such a field were applied to a single domain. This is a fairly easy extrapolation, because the effect of applying an external field to a single domain would be small *except* in the immediate neighbourhood of the Curie temperature, where the effect of thermal agitation and exchange interaction are very evenly balanced, and the effect of an applied magnetic field becomes proportionately more and more important. It is also possible to infer the spontaneous magnetisation from the so-called magnetocaloric effect, the increase in temperature on magnetisation.

The agreement between these two quite distinct methods is satisfactory except in the immediate neighbourhood of the Curie temperature. The observed curves never fall abruptly to zero, but approach the temperature-axis exponentially (somewhat in the manner of the Bragg ionisation-distance curve for an alpha particle in a gas). Such behaviour is not predicted by any theory, and it is, at present, a disputed point whether this "foot" represents a real effect that a theory might be expected to predict, whether it points to the occasional existence of "rogue" domains with somewhat higher Curie temperatures, or whether it is to be attributed simply to the existence of small quantities of still ferromagnetic impurity. (Ferromagnetic inclusions might, because of the high susceptibility of the surroundings, surround themselves with highly magnetised regions, and the measured magnetism would be out of all proportion to the quantities of impurity present.) The criterion of ferromagnetism is ordinarily taken to be appearance of observable hysteresis or field-dependence of the susceptibility and, if the ferromagnetic Curie point is defined in either way, it does lie on a reasonable extrapolation of the spontaneous magnetisation curve (the "foot" being disregarded in the same sort of way that one can define an "extrapolated range" from a Bragg curve). Leaving aside this doubtful point, it is of interest to examine the data for nickel, Weiss and Forrer (1926); iron, Potter (1934); the cubic modification of cobalt, Myers and Sucksmith (1951); and 27·5 per cent Cu-Ni alloy, Sucksmith *et al.* (1953) (fig. 29). It is at once quite obvious that no "law of corresponding states", that we should predict on the basis of any "one-parameter" theory like that of Weiss, can apply to all these cases.

The Weiss curve agrees fairly well with the experiments for cobalt and nickel if we put $J=\frac{1}{2}$, that is, if we attribute the magnetisation entirely to single spinning electrons. The agreement is less good for iron, and the disagreement is very marked for the copper-nickel alloy. As we have pointed out already, the Weiss theory is based on assumptions of about the same degree of crudity as is the van der Waals theory, and what is surprising is *not* that such theories fail to reproduce the experiments completely accurately, but that they work as well as they do.

As this point seems to be insufficiently appreciated in the ferromagnetic case, it is instructive to collect from the literature the various alternative explanations of the departure of the spontaneous magnetisation from the simple theory, and of the closely related fact that the "Curie line" is not accurately straight in the immediate neighbourhood of the Curie point.

(a) Néel (1934) extended the Weiss theory by his hypothesis of the "fluctuations of the molecular field". Physically, this amounts to introducing, besides a "long-range" interaction of Weiss-type a "medium-range" interaction supposed to act between groups of N

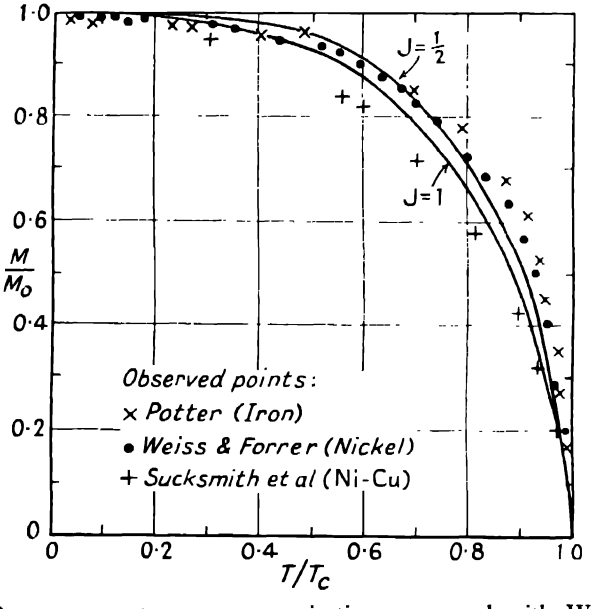

Fig. 29. Data on spontaneous magnetisation compared with Weiss theory. Curves according to Weiss theory: $\mathcal{J}=1/2, \mathcal{J}=1$.

atoms. N was chosen as 750 in order to get the best fit with the experimental data on the curvature of the Curie line for nickel. This certainly represents an improvement on Weiss's original theory, in that account is taken of the fact that any actual interaction *must* be of finite range, but the range indicated by such a choice of N seems altogether too large for exchange-type interactions. To fit all the data, it was also necessary to suppose that the "effective number of magnetic carriers per atom" was itself a function of the magnetisation. We thus have, in effect, *three* adjustable constants instead of the *one* used by Weiss, and considerably improved agreement with experiment could be obtained whether or not the extra constants had any physical meaning. As in

Bethe's (1935) model, Néel found part of the specific heat anomaly persisting above the Curie point.

(b) Becker and Döring (1949) point out that a model of Weiss type ought, logically, to be supplemented by a consideration of the effect of "cluster-formation" (Schwarmbildung). As we have already seen (p. 135), any ferromagnetic interaction should lead, not only to a *preponderance of the number* of atomic magnets of one sign within each domain but the *arrangement* of the "positive" and "negative" magnets in any one domain will be striving towards an ordered pattern. Becker and Döring, *Ferromagnetismus* (1949), p. 41, consider the effect of this semi-quantitatively, and show that it is capable of leading to results very similar to Néel's (1934).

(c) A result qualitatively similar to Néel's results could also be obtained from Bethe's model (1935) or Kirkwood's model (1938)

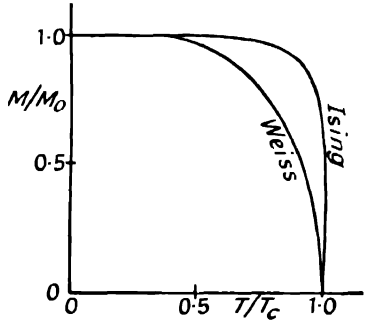

Fig. 30. Spontaneous magnetisation according to Ising and Weiss models for plain square lattice.

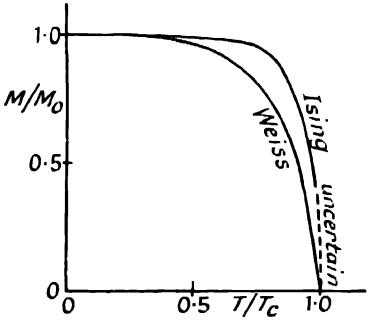

Fig. 31. The same for simple cubic lattice (Wakefield's calculation).

where we can, if we wish, treat z, the "effective number of neighbours" as an adjustable constant measuring the effective *range* of the interaction instead of fixing it according to the lattice structure, as is usually done for *alloys*, for which a "nearest-neighbour" approximation is probably very good.

(d) Better agreement with the results of Sucksmith *et al.* (1935) for Ni-Cu alloy could be obtained by assuming a larger value of $\mathcal{J}$ than $\frac{1}{2}$, and replacing the hyperbolic tangent function by the appropriate Brillouin function. One might try $\mathcal{J}=3/2$ or $5/2$ for the alloy Ni-Cu but there seems to be no very good reason for doing this, and yet for retaining the value $1/2$ for pure nickel. In any case this change is in the wrong direction to account for the results for iron, Potter (1934).

(e) Some indication of the effect of *shortening* the effective range of the interaction can be obtained by comparing the results for the Ising model in two and three dimensions with those of the Weiss model

(figs. 30 and 31). (See Brooks and Domb (1951) for the spontaneous magnetisation and Curie line for the Ising model in two dimensions, and Wakefield (1951) for the spontaneous magnetisation for the simple cubic lattice—estimated, but almost certainly nearly correct). The extreme shortening of the effective range of interaction results in the spontaneous magnetisation curve becoming much steeper near the Curie point, and in a strong curvature of the Curie line. These changes are in the *directions* required to explain the trend of the spontaneous magnetisation curves, particularly of iron, and the curvature of the Curie line, but the assumption of strict nearest-neighbour interactions is obviously too drastic.

(f) As we have already mentioned above (p. 196) a theory of Stoner type (1938) results in a slight curvature of the Curie line, possible incomplete saturation at $T=0$ and quite a variety of possible spontaneous magnetisation curves, according to the precise assumptions we make about the band structure. The departures from the Weiss model here result, not from shortening the *range* of the interaction, but from permitting the magnetic carriers to move through the lattice. Very recently Hunt (1953) has claimed to show that even better correlation of the experiments can be obtained by introducing an I^4 term into the exchange energy in a Stoner model, as suggested theoretically by Wohlfarth (1953).

It is, of course, not intended to suggest that all of these points of view are mutually antagonistic and inconsistent, indeed many of the approximate treatments can be considered to be attempts to allow for the finite range of the actual interaction between atomic magnets. Nevertheless, comparison of the above treatments seems to show quite clearly that the curvature of the Curie line, and the departure of the spontaneous magnetisation curve from the ideal Weiss one with $\mathcal{J}=\frac{1}{2}$, could, in principle, be regarded as measures of any one of at least *four* quite distinct physical quantities, and there seems, at present, no means in sight of deciding their relative importance experimentally. These quantities appear to be:

(1) The "effective range" of the interaction. (In the present state of knowledge we cannot define this quantity precisely.)

(2) The "directional anisotropy" of the interaction (pp. 182–92). We shall see later that some anisotropy is required by domain theory, and we must try and strike some balance between Ising (1926) and Bloch (1930) type models, the Bloch model representing complete isotropy, the Ising model strong anisotropy.

(3) The "effective quantum number" of the magnetic carriers (p. 202).

(4) The "mobility" of the magnetic carriers. One arrives at this conception by comparing Stoner's (1938) and Heisenberg's (1928)

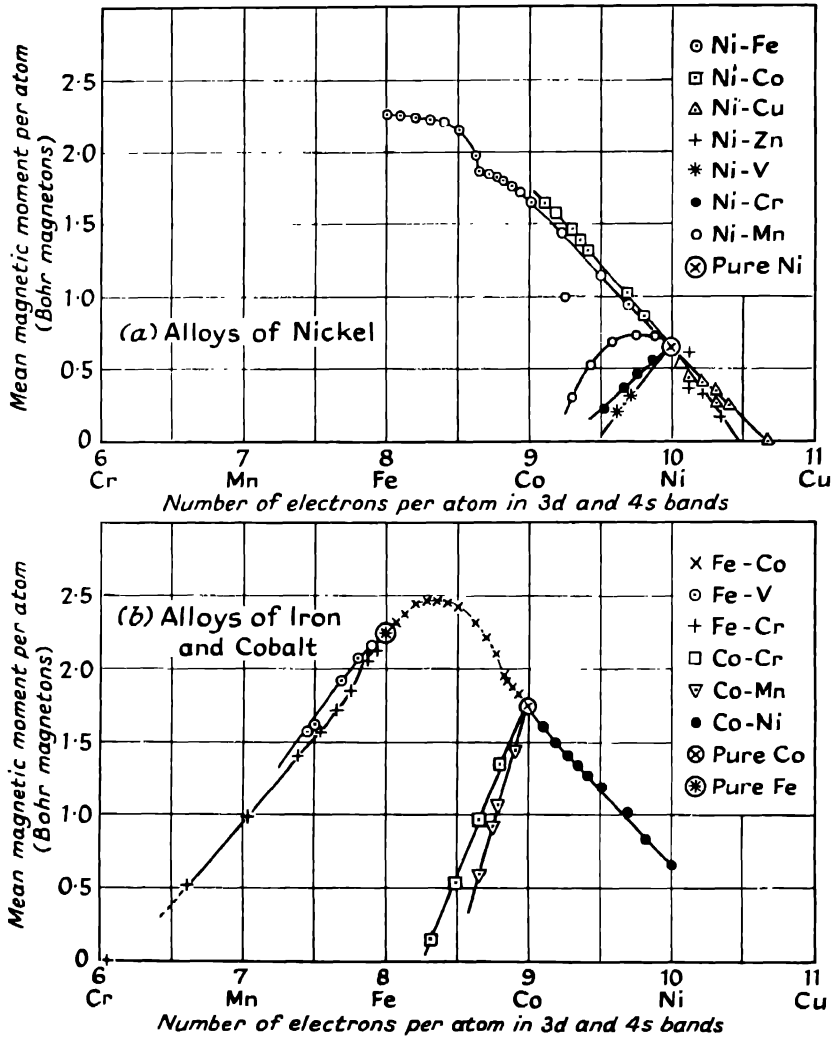

Fig. 32. Atomic magnetic moments of binary alloys as functions of composition. Data collected by R. M. Bozorth (1950), *Phys. Rev.*, *79*, 887.

models. Some compromise will have to be struck between them, possibly on the lines indicated by van Vleck (1953). We cannot assign a numerical measure to "mobility" yet, because we only know how to treat extreme cases.

The author regards the following points as established with reasonable certainty: At very low temperatures the Bloch model (1930) is, on both theoretical and experimental grounds, probably preferable to any of the

others, but it becomes useless near the Curie point, and we are at present without news on how to link it up with any of the other points of view. It is to some development of Stoner's point of view (1938) that one looks most hopefully for such a link-up, and Stoner's explanation of partial saturation at absolute zero, in terms of a partly oriented band, seems the only theory that can, at present, account for the well-known discrepancy between the slope of the Curie line and the "final saturation" as $T \to 0$ (p. 195).

Sucksmith *et al.* (1953) consider that only a few data exist from which reliable results for the spontaneous magnetisation of alloys can be extracted. According to the "band" picture of metals, the main effect of alloying is to change the number of electrons present in the "conduction" or "valency" bands as compared with the pure metal, and a systematic study of the effect of this "change of effective number of electrons" on the spontaneous magnetisation curves ought to give us valuable clues about the real mechanism of the interaction responsible for ferromagnetism. Data collected by Bozorth (1950) show (fig. 32) in a very elegant way the relevance of the band model. The atomic moment is determined by the slope of the Curie line, and the alloying of a ferromagnetic with other metals containing a greater or smaller number of electrons in the 3*d* and 4*s* shells (which hold just 12 electrons when full) reduces or increases the mean magnetic moment per atom. The variation of this magnetic moment with concentration of the alloying metal is nearly always linear, and the slope has always about the magnitude and sign that one would expect on the simple band picture. If too much of the "foreign" metal is added, the lattice structure is liable to change, or order-disorder effects may set in (this is probably the explanation of the marked curvature shown in the Ni-Mn series). In such cases the simple linear law cannot be expected to hold.

7.5. The "Spherical" Model of a Ferromagnet

Our survey of existing theories has revealed as one of the most urgent needs some means of allowing for the changes to be expected in the statistical mechanical consequences of a theory as a result of lengthening or shortening the "effective range" of the interaction. There is also, as we shall see below, an almost equally urgent need to be able to determine the consequences of an interaction that changes sign at some critical distance (p. 218). A treatment has recently been found, Montroll (1949), Kac and Berlin (1952), which promises to give considerable information on such points, and also on the effect of replacing anisotropic by isotropic interactions, etc. (Wannier (1952) has pointed out that a very considerable shortening of the original treatments resulted if the grand partition function was calculated instead of the ordinary one.) These treatments do give models showing a transition involving an analytic

discontinuity, but they are, at present, far too crude to permit any quantitative comparison with experiment. (The predicted specific heat is actually *constant* (not zero) below the transition temperature.)

Very briefly, if we have the "generalised Ising model", in which we have to determine the partition function,

$$\sum_{\mu_j} \prod_{j} \exp \{H^{(l)}(\mu_j \mu_{j+l}\} \tag{29}$$

subject to the auxiliary conditions $\mu_j{}^2=1$ or $\mu_j=\pm 1$ (30)

where $H^{(l)}$ is proportional to the interaction of two magnets a distance l apart, we replace the very stringent auxiliary conditions (30) by the much weaker one

$$\sum_{1}^{N} \mu_j{}^2=N \tag{31}$$

After a suitable choice of the energy-zero to make the $H^{(l)}$'s such that the quadratic form in (29) is negative definite, we can find a linear transformation of the μ_j's to reduce the quadratic form occurring in (29) to a sum of squares, and the summation over the two possible values of μ_j is replaced by an integration from $-\infty$ to $+\infty$ for each μ_j, which can be carried out in finite terms, subject to the auxiliary condition (31). This new auxiliary condition means that, on each lattice point, we allow *any* number of magnets (integral or fractional), subject only to the condition that the *total* (magnetic moment)^2 on all lattice points adds up to the correct value. The important point is that one can examine quickly the effect of using different "interaction functions" $H^{(l)}$ *without* seriously complicating the work. It would be possible to introduce more restraints on the μ_j's than the one restriction (31), but complications increase rapidly if we do this.

These weaker assumptions would make the model physically inadmissible for most of the applications of the Ising model and Weiss model that we made in Chapter VI (e.g. the whole essence of the "cell" model of a liquid is destroyed if we are going to admit configurations in which one "cell" contains a very large number of molecules—and a similar remark applies to the "sites" in the order-disorder problem), and for this reason, this model was not mentioned in that chapter. The model does seem to have rather more relevance to the magnetic case, for which the implied assumption that large numbers of electrons can occasionally congregate in small volumes of the metal does not do quite so much violence to the physics of the problem. We can only await with interest any further developments in the mathematical technique, enabling us to impose rather more realistic restrictions on the μ_j's than that implied by (31). Even as it stands, the model is not as artificial as at first appears, such ludicrous cases as those in which a few lattice

sites each contain $\sim N^{1/2}$ magnets are *permitted* by (31), but such configurations contribute very little to (29) because of the relative smallness of the corresponding Boltzmann factors compared with those for a more even distribution of magnets.

7.6. The Domain Theory of Ferromagnetics

We shall consider in this book only irreversible effects associated directly with the existence of domains. For an account of various effects, involving time-lags in magnetisation as distinct from true hysteresis, the reader is referred to Becker and Döring's later chapters (1939).

The idea that a ferromagnetic consists of spontaneously magnetised domains arranged in such a way as to give an apparently unmagnetized state of minimum free energy is due to Weiss (1907), but it was not until some time after Heisenberg's (1928) work on exchange effects that the theory could be put on a proper basis. The theory can be developed in a way that is independent of the precise quantum-mechanical origin of exchange effects, it being only assumed that they are described, at least to a first approximation, by a scalar product expression of the type (10), the exchange integrals, whatever their origin, falling off fairly rapidly with increasing distance. Although the theory of "domain walls" is related in some ways to the spin-wave theory of Bloch (1930), it can be carried through even if the temperature is too high for the latter theory to be properly valid. The theory of domains falls naturally into three parts:

(a) The physical reasons why domains exist at all. This question is very far from trivial, and the explanation has been found to depend on the interplay of a number of different factors. Associated with this question is the probable nature of the transition region between two domains, usually referred to as a domain "wall".

(b) The manner in which domains are likely to arrange themselves in an actual specimen in order to have the lowest possible free energy.

(c) The manner in which domain boundaries are likely to move in response to changes in applied magnetic fields. The main problem here is the explanation of the coercive field, but the discussion also yields information helping in the interpretation of all parts of the hysteresis curve of an actual material.

The historical development of the theory is not quite what one might have expected, item (b) having lagged considerably behind item (c) instead of preceding it. This is simply because one cannot see directly the domains inside a specimen, and it has gradually become clear that inferences from the "Bitter patterns" (the patterns that appear on a magnetised specimen, for example, small particles of iron are scattered

over it) can be a most misleading guide to the actual sizes and shapes of the domains unless the surface of the specimen is extremely carefully prepared. Elmore (1937; 1938), Williams, Bozorth and Shockley (1949). (See also Kittel's review article (1949).) For theoretical work on the expected domain patterns of minimum energy see Néel (1944).

7.6.1. What determines the Size of a Domain?

The answer to this question is fairly simple to state, the ultimate reason for the existence of domains is that, in a ferromagnetic, we are concerned with two quite distinct types of interaction involving the spin directions of the electrons, the exchange effect, and the direct magnetic interaction between dipoles. Although the magnetic interaction is numerically very much smaller, the competition between the two is not so one-sided as one might, at first, expect. The reason for this is that the interaction between magnetic dipoles falls off only as the inverse cube of the distance, and this means that configurations can be found which, for an infinite specimen, would lead to an infinite energy per atom. Put in another way, the magnetic energy, associated with a given value of I, depends on the size and shape of the specimen. This situation can be described in various ways, by introducing such ideas as the "demagnetising coefficient", the appearance of "magnetic poles" on the surface of the specimen, or the Lorentz "local field", all of which are equivalent to the statement that there is a magnetic interaction per unit volume varying as I^2, the constant of proportionality depending on the shape of the specimen, and on the variation of I with position. Now, if we suppose that the "exchange interaction" only extends over a few lattice distances at most (and a result like this must follow from practically any theory that attributes it to "overlap" of wave functions), it becomes clear that we can make a net gain of energy if we replace a single large domain by some alternating pattern of "positively" and "negatively" magnetised domains. The reduction in magnetic interaction is proportional to the *volume*, while the increase in exchange interaction is proportional only to the number of "wrong" pairs of nearest neighbours introduced, which will be proportional to the total *surface area* of the domain boundaries. (The assumption that these boundaries are *abrupt* will be reviewed in a moment.)

We can make a simple calculation of the energy gained by introducing a domain-structure with about N boundaries per centimetre, as follows: The magnetic energy per unit volume is of the order of I^2/N, and I is of the order of 10^3 e.m.u. The exchange energy is proportional to N, the energy associated with forming a boundary being of the order of 1 erg/cm^2. Thus we can determine N (in order of magnitude) by minimising the sum

$$N.1+I^2/N \text{ ergs/cm}^2=\text{minimum} \quad \text{or} \quad N\sim 10^3$$

which suggests that domains should have linear dimensions $\sim 10^{-3}$ cm or between 10^4 and 10^5 lattice distances. Thus, the *existence* of domains is a consequence of the magnetic interaction being of *longer* range than the exchange interaction. (See p. 117.)

We can, however, economise in exchange energy, without making any significant change in the magnetic energy, by making the "wall" between two domains *gradual* instead of abrupt. We replace the abrupt boundary, dividing "positively" and "negatively" oriented spins by a transition region, or "wall" of n layers, the spins in each layer being nearly parallel to one another, but inclined at an average angle of π/n to those in the preceding and following layers. Instead of the energy $2\mathcal{J}(1-\cos\pi)$, which would have to be supplied if two neighbouring spins were placed in opposite directions, we should have instead $2\mathcal{J}n\{1-\cos(\pi/n)\}$, which would result if the "wall" were spread out over n lattice distances, each spin being inclined to its neighbour at about the same angle. Thus, the "spreading-out" process will always reduce the energy required, and, for n large, the energy per "wall" is proportional to $1/n$. Thus, there is a clear gain of energy by making the "wall" gradual, and doing this should have no significant effect on the magnetic energy. In fact, if the magnetic and exchange effects were the only ones involved, it would take very little energy to create a domain "wall", and we should get a minimum of energy when n took as large a value as would be compatible with the assumed value of N, that is, our final state of affairs could be described colloquially as "all walls, smeared-out domains". In fact, it *is* possible to realise such a situation experimentally in certain cases, as we shall see below (pp. 212–17).

7.6.2. What determines the Thickness of the Wall?

There are, however, two further effects that we must allow for before we can build up a complete picture. Although they are hard to compute theoretically, the quantities concerned can be measured experimentally. These effects are magnetic anisotropy and magnetostriction.

Experiments with single crystals have shown (see fig. 33) that all three ferromagnetics have considerable anisotropy, and that it may take considerable energy to saturate a crystal along any direction that differs from one of the "easy" directions. For iron, the easy directions are the cube edges, for nickel the cube diagonals and for cobalt, which has hexagonal symmetry, the hexagonal axis. No such effect is predicted for a system of pure electron spins in a crystal of cubic symmetry, and it is

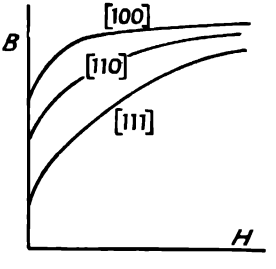

Fig. 33. Magnetism curves for single crystals of iron.

necessary to suppose that there is an interaction between spin and orbital magnetic moments, the latter being subjected to the electric field of the crystal lattice. The orbital magnetic moment can only make a small *direct* contribution to the magnetic moment of a crystal (because of the observation of a value of very nearly 2 per the gyromagnetic ratio for all three ferromagnetics), but this *indirect* effect is possible. The reader is referred to Brooks (1940) for details. See also Fowler, *Statistical Mechanics* (1936). The existence of the anisotropy tends to limit the thickness of a domain "wall" for a fairly obvious reason, namely that, supposing that we start with two domains magnetised in "easy" directions, the creation of any gradual "wall" of finite thickness between them necessarily involves turning nearly all of the spins in the "wall" *away* from the directions of easy magnetisation, and this requires the *expenditure* of energy, which has to be set against the *saving* of energy that, for the reason explained above, results from making the "wall" thicker. The energy associated with the anisotropy increases with increasing n, while the energy associated with the exchange effect proper is proportional to $1/n$, so that the energy of a "wall" will be a minimum for some finite value of n. Actually the assumption that the relative inclination of the spins between each pair of neighbouring "layers" in the wall is the same does not lead to quite the lowest possible energy. Becker and Döring (1939), p. 191, show that an even better value of the total energy can be obtained by assuming instead a law of the type

$$\tan(\tfrac{1}{2}\theta)=\exp(x/x_0) \qquad (32)$$

where $x=0$, $\theta=0$ represents the centre of the "wall", x is a co-ordinate perpendicular to the wall, and x_0 an "effective thickness", taking the place of n as used in the cruder calculations. The result of the more accurate calculation differs from the crude one only by a numerical factor. (The behaviour of θ as a function of x is not at all unlike that of a function of hyperbolic tangent type. If the anisotropy is given, we can estimate the energy of a "wall" by minimising with respect to x_0 or n.) A large anisotropy implies a *thin* "wall" of *high* energy (p. 192).

7.6.3. The "Ideal" Hysteresis Curve

If the anisotropy existed by itself, we should predict a domain wall of finite effective thickness, therefore one that would need the expenditure of *finite energy* for its creation. This leads to the fundamental result that, starting with a specimen completely magnetised along an "easy" direction, we cannot create in it a nucleus magnetised in any other of the "easy" directions without creating one or more domain walls. Thus, under "ideal" conditions, having applied to our specimen a field large enough to wipe out any domain structure, we might expect to be able to drop the field to zero (point D, fig. 34) and yet still to

keep the specimen magnetised practically to the spontaneous magnetisation appropriate to the particular temperature. Although it is thermodynamically profitable to change this to a structure with net magnetisation zero, containing domains, this cannot be done without creating walls and this needs some energy. The probability of a domain, containing something of the order of 10^8 or 10^9 atoms, forming by a spontaneous fluctuation is too remote to be worth considering, and the only practicable way of forming one or more domains is to apply a field in a direction *opposite* to that originally applied. At a certain field (point C, fig. 34) it becomes energetically profitable for some of the spins in one layer of atoms to turn *into* the reversed field, even though they must first go through a "difficult" direction of magnetisation, and even though their reversal must also result at first in these few spins having a high exchange interaction with their neighbours. Once this stage is reached, there is no further energy barrier to be surmounted. The subsequent processes, a change of the *abrupt* boundary surrounding the few reversed spins into a *gradual* wall, followed by expansion of the small reversed domain until it fills the whole specimen, both of them result in gains of energy, and would proceed even if the field were not altered further. Thus, if we had just the three effects of exchange and magnetic interactions, together with the magnetic anisotropy, the predicted hysteresis curve would be almost rectangular, as is shown in fig. 34. The remanence would be precisely equal to the spontaneous magnetisation at $H=0$ appropriate to the temperature, as calculated from the Weiss or other appropriate model. Because of the large numerical value of the exchange interaction the effect of a magnetic field on the magnetisation of a domain is small, so the slope of the line, AC, will be small. The coercive field, H_c, in fig. 34 is to be calculated in the manner already outlined, by balancing the anisotropy energy necessary to create a pair of walls against the gain in magnetic energy resulting from reorienting the corresponding number of spins. The reader is referred to Becker and Döring (1939) for an account of the considerations that govern the *growth* of nuclei of "needle" and "disc" shapes, once they are formed.

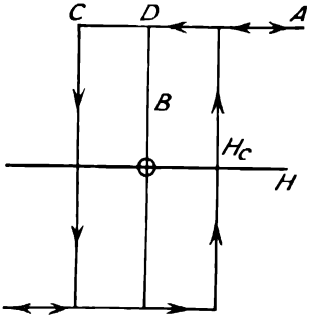

Fig. 34. "Ideal" hysteresis curve. (Uniform tension.) No anisotropy.

7.6.4. The Effect of Magnetostriction

In practice a hysteresis loop such as that shown in fig. 34 is only observed under very special conditions, and it is fairly easy to understand the effect of magnetostriction, which we shall now consider, in

"rounding off the corners" of the hysteresis loop, and in making its form sensitive to the precise way in which the specimen is prepared and annealed. Since magnetostriction implies that changes in magnetisation are associated with mechanical stress and vice versa, it follows that a tension applied along one of the "easy" directions of magnetisation may make magnetisation in this direction (as compared with other directions) energetically less profitable or energetically more profitable, depending on the *sign* of the magnetostriction coefficient. Thus, if we had a perfectly uniform specimen, we should be able to increase or reduce the effective energy of anisotropy at will, simply by varying the tension. If the magnetostriction coefficient is *negative*, as it is in nickel, tension along an "easy" direction tends to *reduce* the difference in energy between a domain magnetised in this easy direction and in one of the difficult ones. The result should be to *increase* the thickness of the "walls" (with no anisotropy they should fill the entire domains), but at the same time to *reduce* the energy required to form them, and thus to reduce the coercivity. If the magnetostriction coefficient is *positive*, as occurs with iron and cobalt, applying tension along an "easy" axis should *increase* the effective anisotropy, the "walls" should become *thinner*, the energy necessary to create them should *rise*, and the coercivity should be *increased*. The magnitudes, and even the signs, of the magnetostriction coefficients are hard to predict theoretically in the present state of our fundamental knowledge, so it is probably best to take them as data. The physical reason for their existence is fairly obvious, they will arise mainly from the variation of exchange interaction when the lattice distance is changed.

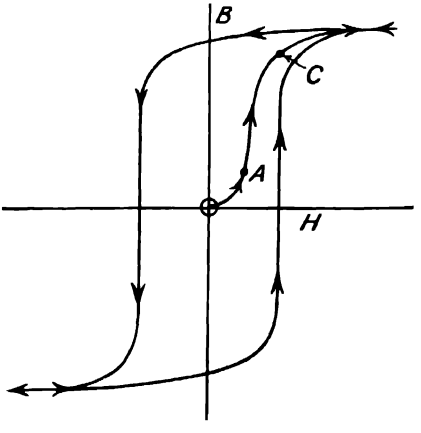

Fig. 35. Modification of ideal hysteresis curve due to magnetic anistropy and reversible effects.

Both these predicted effects of tension have been confirmed in practice. Under a sufficiently large tension, the coercivity of a nickel wire practically disappears, while the hysteresis loop of an iron wire is rapidly "opened out" into something very closely resembling the "ideal rectangle" of fig. 34. The meaning of the hysteresis curve obtained with an ordinary specimen is now readily understood qualitatively. The fields necessary to create reversed domains and the corresponding pairs of "walls" vary from point to point in the specimen,

due to inevitable local stresses, and also because not all the crystallites are oriented in the same direction. We can thus explain qualitatively the "steep" part of the hysteresis loop and the associated Barkhausen effect. The typical process would be the formation of a fresh domain and pair of "walls", each of which would "run" through the specimen until it reached a crystal boundary, or some region of very high or very low local stress which made it unprofitable for it to run further. A further change in the applied field may result in some more domain "walls" being formed and beginning to run through the crystal, until they too are stopped by some irregularity and so on. It is only when we apply a sufficiently high external tension that the various local stresses are "ironed out" so that we finally get a rectangular hysteresis loop, but the "rounded corners" (fig. 35) are still present.

7.6.5. The Experiment of Sixtus and Tonks

These considerations are strikingly confirmed by the famous experiment of Sixtus and Tonks (1931) in which domains of macroscopic size were produced in wires under tension, magnetised longitudinally. When the tension was fairly high, so that the hysteresis loop was practically rectangular, they found indeed that the domains were of macroscopic size, so that it was possible to do the following experiment: Magnetise the wire to saturation, reverse the field acting on the whole wire and set it at a value numerically just below the coercive field. With the aid of auxiliary coils the field could be increased locally until a pair of "walls" *could* form, whereupon the reversed domain would begin to expand, and the progress of a "wall" through the specimen could be followed by means of search coils. Measurements of the velocity of propagation gave a law of the type

$$v \propto (H - H_0) \tag{33}$$

where H_0 is very much less than the field H_c, the coercive field, the latter being, as we have seen, a measure of the energy needed to create a pair of "walls". Once created, the "walls" can "run" in fields decidedly less than H_c, but the "critical field" H_0 can never be reduced absolutely to zero. H_c is described by Becker and Döring as the "starting field" (Startfeld).

The form of equation (33), and the existence of the field H_0, can both be interpreted readily, though H_0 is hard to predict theoretically. Since there will always be some inhomogeneities of tension, impurities in the lattice, etc., the energy of a boundary will not be quite constant, but will vary somewhat from place to place, in the manner suggested in fig. 36. On arrival at a point such as A, at which the energy of the wall is a minimum, there is no reason for it to run any further if the applied field H is zero. But, if H is finite, we have to balance the energy

necessary to move the wall from A to a point like B against the gain in magnetic energy that results from a further travel of the "wall". In this way it is possible to understand the existence of a minimum field H_0 which has to be present in order that the boundary can continue moving at all. The linear law (33) for the velocity at higher fields also receives a natural interpretation, it is simply associated with *eddy-current damping*, the reversal of some of the atomic magnets inducing a current, the field due to which current is, by Lenz's law, in a direction tending to *stop* the motion of the "wall", so that the forward motion of the "wall" is governed by the decay of these eddy currents. Insertion of numerical values shows that this explanation gives velocities of the correct order of magnitude, though the existence of other damping mechanisms is, of course, not excluded. Various workers have pointed out that an "effective inertia" of the walls might result from gyroscopic effects associated with the angular momentum of the electrons forming the "wall", so that the equation of motion may contain an inertia term also.

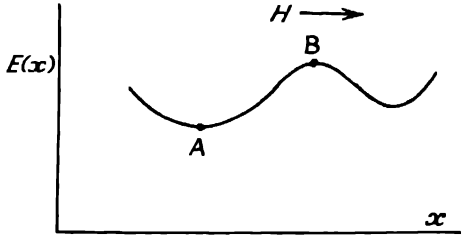

Fig. 36. Probable variations of energy of domain wall as it moves through specimen.

We now turn to the explanation of the "rounded corners" that seem to persist in our observed hysteresis loop, however high we make the tension.

7.6.6. Reversible Effects associated with Domains

These "rounded corners" can be reproduced fairly reasonably by decreasing and increasing the applied field, that is, they seem to correspond to some *reversible* effects. Even in an ordinary "laboratory" specimen it is usually found that a finite region of the magnetisation curve (near the origin) and a finite region just below "technical saturation" are fairly accurately reversible. Various reversible mechanisms have been suggested which are probably associated with these regions, the most important of which seem to be the following:

(a) The motion of "walls" *between* points like A and B in fig. 36. As long as a field no greater than H_0 were applied, we would simply have the "wall" moving away from A when the field was applied, returning

there when it was removed, the whole process corresponding to reversible conversions of "wall energy", whose origin has already been traced above, into the ordinary magnetisation energy associated with a domain in a magnetic field.

(b) A similar motion of "90° walls", that is to say, "walls" dividing domains magnetised in two "easy" directions at right angles to one another. No change of "wall" energy need be involved here, but, if a field is applied along one easy direction, Boltzmann's expression requires that the total volume of domains magnetised along this direction should increase at the expense of those magnetised along other "easy" directions. It requires further that this difference should disappear again when the field is removed.

(c) The *rotation* of the direction of magnetisation of a domain from one of its easy directions into one more nearly parallel to the applied field.

It is sometimes stated that, of the various characteristic portions of a magnetisation curve (fig. 35), the "initial rise" O to A is associated with mechanisms (a) and (b), the "steep portion" A to C with Barkhausen jumps, that is mechanisms of the type studied in the Sixtus and Tonks experiment, while the "approach to saturation" (point C onwards) is mainly associated with the rotation of the directions of magnetisation. This statement is, however, only a very rough summary of the true position. The reader is referred to discussions by Stoner of the analysis of magnetisation curves (1950; 1953). Although many of the mechanisms are fairly well understood, the sorting out of the reversible and irreversible effects is no easy matter, even with the additional evidence obtained from magneto-thermal experiments.

These mechanisms are all discussed in detail in Becker and Döring (1939) to which the reader is referred for derivations of the formulae involved. A comprehensive review of the whole field has also been made by Kittel (1949). A very large number of quantitative and semi-quantitative formulae have been derived and compared with experiment with varying degrees of success, and considerable further material has been added by later workers, for a summary of which the reader is referred to Stoner's articles (1950; 1953). The situation may perhaps be summed up by saying that, assuming the initial premiss that ferromagnetism is basically due to an exchange interaction of short range, the fundamental principles on which the interpretation of the properties of an actual ferromagnetic material should proceed are known, but that the attempt to apply them to particular cases leads to an investigation that begins promisingly, and then becomes bogged down in a mass of detail. Such a situation is common enough in rapidly advancing fields of knowledge and, as two typical examples, we may mention the problem of the Alnico alloys and the Permalloy problem.

7.6.7. The Alnico Alloys

The characteristic feature of these alloys is the very high *coercivity*, which makes them suitable as permanent magnets whenever the design requires them to have a large demagnetising coefficient. (The *remanences* are *not* particularly high.) We have already seen that the coercivity can be much increased by applying stress to a material, and these alloys may be thought of as exploiting the fact that tensions can be produced within the crystal lattice itself by the process of *precipitation hardening*, that is using a "mix" that corresponds to the coexistence of two or more phases at room temperature, and arranging the heat treatment in such a way that most of the precipitation occurs *after* the alloy is solid. If the lattice constant of the precipitate differs significantly from that of the matrix, relatively enormous local stresses can be set up, and it, at first sight, appears to be a comparatively simple problem to make a numerical estimate of these stresses and to try to correlate this figure with the expected increase of coercivity with stress according to the formulae developed by Becker and his collaborators.

In practice, the problem has turned out to be very much more complex, for it has proved necessary to consider the contributions of the precipitate as well as of the matrix to the magnetic properties, indeed most workers consider that the precipitate makes the main contribution. Now the particles of precipitate appear to be in the range of size for which it is energetically advantageous for each particle to consist of only *one* domain, and the problem that we really have to study is not that of a simple crystal lattice at all, but rather that of an aggregate of needle-like or plate-like particles, suspended in a more or less ordered pattern in a matrix, and it is then not possible to neglect interactions between the particles. The study then becomes similar to that of permanent magnets made up with sintered powders. From the rough calculation that we made above (p. 208) particles of up to about 10 microns in size are unlikely to contain more than one domain. Thus, a rather unexpected shift of emphasis has occurred, the theory of the Alnico alloys, which are so hard as to be almost unmachinable, turning out to be closely related to that of "powder" magnets! For a detailed consideration of such problems the reader is referred to Stoner and Wohlfarth (1948) and to various articles in *Reviews of Modern Physics*, Jan. 1953, especially those by Meiklejohn, Adams and the discussion of these two papers, Geisler, Nesbitt and Heidenreich, and Weil, where many other references to original papers will be found.

7.6.8. The Permalloy Problem

This is another example where some unexpected twists have occurred. In view of the fact that iron has a positive magnetostriction and nickel

a negative one, it is natural to look for unusual effects in an alloy for which the magnetostriction is zero. This occurs at approximately 80 (atomic) per cent Ni (the exact figure being uncertain and depending on precisely *which* magnetostriction coefficient we want to be zero). In fact this is very close indeed to the composition at which maximum initial permeability is attained (78·5 per cent Ni) and it is also close to the composition at which the anisotropy vanishes (75 per cent Ni). This is to be compared with what we have just said about the close relationship of magnetic properties with the ease with which domain boundaries can be *shifted*, controlled mainly by the magnetostriction, and with the ease with which the magnetisation direction can be *rotated* by applying a magnetic field, controlled by the anisotropy.

The especially striking property of alloys of the Permalloy type is an extremely high permeability in small fields, together with a small coercivity, so that these alloys seem to approach the "ideal" behaviour that would be expected of a ferromagnetic according to a simple application of the Weiss theory (which predicts a sudden jump in I in zero field and little change at other fields). If the magnetostriction and anisotropy were both very small, we should get the situation envisaged above (p. 209) in which the domain "walls" would "fade out", that is, attain an effective thickness comparable with the domain size itself, and, at the same time, require very little energy for their creation. Because of the effect of crystal inhomogeneities, it is extremely hard to predict initial permeability numerically. An upper limit to its possible value was obtained by an ingenious argument due to Kersten (see Becker and Döring (1939), p. 154). If the anisotropy is small, the energy required to rotate the magnetisation in a domain depends mainly on the magnetostriction and the tension. Now we can estimate the *minimum* tension likely to exist in a magnetised sample by considering that *some* tension must be caused by the very presence of domains themselves, since they will be oriented in various directions, and the very fact that they are all magnetised itself implies a slight change in the shape of each and thus a stress existing in the material, which may be estimated roughly as equal to λE (λ=the magnetostriction coefficient, E=Young's modulus), which will be present however carefully the material may be prepared. On this basis, Kersten arrived at the formula

$$\mu_{\max} \approx \frac{8\pi}{9} \frac{I_s^2}{\lambda^2 E} \tag{34}$$

I_s=magnetic moment per unit volume existing in a domain

as an estimate of an upper limit for the initial permeability. Since this formula agrees closely with the highest measured values for alloys of several different compositions over a range covering the Permalloy composition, it almost seems as if one need look no further for an

explanation. The fact that the actual maximum permeability is reached at a composition intermediate between that for zero anisotropy and zero magnetostriction also seems to fit in extremely well with the theory.

There is, however, an extremely puzzling fact, namely that the good magnetic properties of Permalloy fail to appear if it is *annealed*, instead it must be *quenched* from at least 600°C. If this is not done, the initial permeability shows only a small improvement over that obtainable at other compositions. This strange behaviour, which seems to cut completely across our ideas just outlined, for annealing always reduces internal stresses, was eventually traced to the appearance of a superstructure of the type Ni_3Fe, the formation of which apparently has to be *prevented* in order to get the high initial permeability. In spite of various suggestions no really satisfactory explanation of this observation has been found, though Bozorth (1953) notes that the quenched alloys near the Permalloy composition show a much smaller anisotropy constant than do the ordered ones, so that it is an observed fact that only by choosing the correct composition and then quenching can one make *both* the anisotropy and the magnetostriction small. However, this effect of the ordering process on the anisotropy is itself something that, in turn, calls for an explanation and none seems to have been found. For fuller discussions, the reader is referred to Becker and Döring, *Ferromagnetismus* (1939), p. 411, and to Bozorth's review article (1953), also Kittel's review article (1949).

7.7. Antiferromagnetism

For comprehensive reviews and bibliographies of this field see Labhart (1953) and Lidiard (1954). An elementary account of the phenomenon is given in Chapter VI (p. 124). It can, as we have seen, be formally described by a natural generalisation of a theory of Weiss type, in which the "effective field" may be described by *three* independent constants. The generalisation of the Ising model is nearly as simple, see, for example, Brooks and Domb (1951). For a lattice such as the plane square lattice we need only reverse the signs of alternate spins and then proceed as for the ferromagnetic. For the body-centred cubic lattice we have two possibilities, either its two simple cubic sublattices may *each* carry an antiferromagnetic pattern, or we may have nearly all the positive spins on one sublattice and nearly all the negative spins on the other. In more complicated crystals, we have to consider the possibility, pointed out by Néel (1948), that the two sublattices may not have equal numbers of sites, a situation which he describes as "ferrimagnetism". Yet another possibility occurs, for example, with the plane triangular lattice, because of the fact that closed paths can be drawn in such a lattice containing odd numbers of "links". The effect of this is to destroy the symmetry between the ferromagnetic and

antiferromagnetic partition functions. In the plane square, and simple cubic lattices, reversing the sign of the interaction does not affect the partition function, the specific heat anomaly, nor the degree of long-range order (provided that the last quantity is suitably re-defined), but this symmetry *is* destroyed in the plane triangular lattice. If all three interactions are equal and antiferromagnetic, the transition temperature is depressed to absolute zero and such a model still has a finite entropy there, Wannier (1950). Other special cases show a similar behaviour, Houtappel (1950).

7.7.1. Mechanisms causing Antiferromagnetism

In principle, there are three mechanisms definitely known that could cause antiferromagnetism, pure magnetic interaction, pure exchange interaction, or the "superchange" mechanism of Kramers (1934), the last being a lining-up of two electrons on different atoms by virtue of their interactions with a third atom. For summaries of the experimental data the reader is referred to Kittel, *Solid State Physics*, p. 187, and Bizette (1951), also to review articles by Labhart (1953) and Lidiard (1954). One might expect the experimental findings to be very much the same whether the interactions were purely magnetic, or purely exchange or some combination of the two. The only cases in which the magnetic interactions are likely to be the dominant mechanism seem to be the paramagnetic alums, and other salts with fairly widely separated ions, used in magnetic cooling. Even with such salts, it is extremely difficult to be certain whether exchange effects are important or not, owing to difficulties in estimating the precise variation of the latter as a function of distance, and further complications may be caused by the effect of the electric field of the water molecules in the crystal.

We shall summarise the few effects that might be expected to occur in the magnetic but not in the exchange case, apart from which it is not necessary to discrimate between the two mechanisms. Since the intensity of magnetisation is never very large, there will be nothing in the antiferromagnetic case corresponding to the complicated interplay of magnetic, exchange and magnetostriction effects that led to hysteresis in the ferromagnetic case. Thus, in developing the theory, it will be nearly always satisfactory to assume an exchange type of interaction, magnetic effects, if they are important at all, merely resulting in small corrections.

7.7.2. Purely Magnetic Interactions

The existence of a Curie point has been established for most salts used in magnetic cooling. A typical substance is ferric ammonium alum, for which the specific heat curve is sketched in fig. 37. The smooth "bump" is associated with the Stark splitting of the ionic levels by the

crystalline field, while a typical Curie point occurs at a somewhat lower temperature. It is feasible to reduce the temperature still lower if a sufficiently high initial field is used, but measurements of the temperatures become difficult. Above the Curie point one can define a scale of temperature in terms of the inverse susceptibility, and one then determines corrections thermodynamically, these usually amounting to only a few per cent. Below the Curie point, the corrections become of major importance, as one might expect. Various methods of making the corrections have been worked out, but will not be discussed here. For an account of the principles involved see Fowler and Guggenheim, *Statistical Thermodynamics*, Chap. XIV.

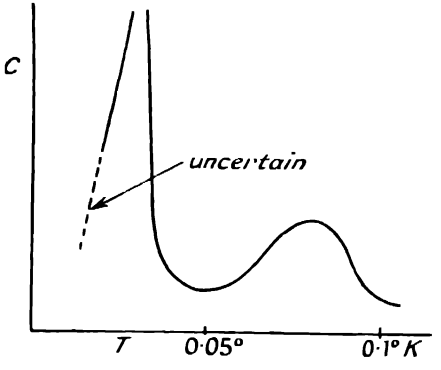

Fig. 37. Specific heat of iron alum.

The nature of the ordered state below the Curie point is not precisely known. It seems to have some properties resembling the ferromagnetic state, for example remanence and hysteresis appear, but the apparent saturation may be only a few per cent of what would be expected if *all* the magnets were lined up. Moreover, there is evidence that the magnetic properties depend on the shape of the specimen. Such "mixed-up" behaviour is very much what would be expected if the interactions were predominantly magnetic, but would be hard to understand if they were predominantly exchange. The differences arise because of the peculiar property of magnetic interactions namely that, see fig. 38, there is a potential barrier between the two possible configurations of lowest energy (a) and (c), configuration (b) (and all other configurations) having higher energy. With interactions of exchange type, there is no such barrier, configurations (a), (b) and (c) having the same energy. This effect is actually the basis of Ewing's (1890) famous attempt to explain hysteresis by means of his "compass-needle" model, but this is not admissible for a ferromagnetic metal, for which exchange effects are responsible for the ferromagnetism.

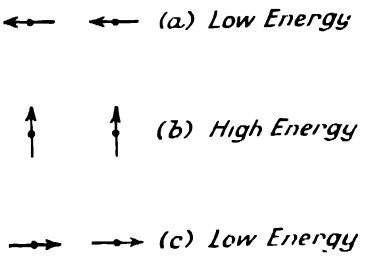

Fig. 38. A peculiarity of dipole-dipole interactions.

If the interactions are predominantly magnetic, we should expect the

state of lowest energy of a spherical specimen to be antiferromagnetic, consisting of alternate *strings* of oppositely oriented dipoles, Sauer (1940), Luttinger and Tisza (1946), but, because of the effect of the different demagnetising coefficient, an elongated specimen would have a lowest state showing spontaneous magnetisation. Furthermore, such an assembly would behave towards a magnetic field in a manner quite analogous to that of the "compass-needle" model, namely, a partially magnetised state imposed by an applied magnetic field would *not* necessarily disappear completely when that field was removed, even though a state with I zero was more stable. The existence of these potential barriers, together with the fact that all treatments of ordering phenomena (except the very crudest) predict the survival of some degree of "ordering of neighbours" above the Curie point, suggests that some traces of hysteresis might survive even here. In fact, behaviour typical of hysteresis effects *was* found in iron ammonium alum by Shire and Barkla (1939), up to several times the Curie temperature, using low-frequency alternating magnetic fields. This can be quantitatively explained on the above basis, Temperley (1940).

7.7.3. Recent Developments

As we have already pointed out (p. 124), *any* type of antiferromagnetic interaction could, to a first crude approximation, be described by a "two-sublattice" model of Néel type (1936), the finer details of the interaction function mainly influencing the precise way in which the lattice divides up, without affecting the formal statistical results. A number of studies of the expected behaviour of such an assembly in the presence of a magnetic field have been made, and we must at least distinguish between the cases in which the field is perpendicular to the direction along which the spins are pointed and those in which it is parallel to that direction. In the former case, the symmetry between the two sublattices will remain, in the latter it will be destroyed. A calculation of the parallel and perpendicular susceptibilities for such a model was made by van Vleck (1941) and a special feature is the characteristic maximum in the parallel susceptibility that would be expected at the transition temperature. For a review of work based on the Néel and similar approximations see, Smart (1953).

One very interesting question that arises is the possibility of the transition between different types of ordering. Smart (1953) shows generally that such an effect is not to be expected in zero magnetic field if the "molecular field constants" *are* really constant, but that it does immediately become possible if these constants do vary with temperature. (This would be an instance of the type of transition foreseen as a possibility by Tisza (1949) (see also p. 16).) The transition from one type of antiferromagnetic ordering to another might be hard to detect

experimentally, but a transition from ferromagnetic to antiferromagnetic seems to occur for MnAs (Serres (1947)) and MnBi (Guillaud (1951)), and such an occurrence can be formally described by means of Smart's (1953) phenomenological picture, though only speculative reasons for such an occurrence can be given at present.

A different type of antiferromagnetic transition can be predicted from a Néel-type model, namely that, in a sufficiently strong external field, the antiferromagnetic state should be destroyed. As it is also destroyed by thermal agitation, one would expect the antiparallel state to be stable only within a closed region in the *H-T* plane, Sauer and Temperley (1940), Ziman (1951), Garrett (1951), Gorter and Haantjes (1952). The approximate behaviour to be expected is shown in fig. 39, the shape of the boundary-curve differing according to the precise model used. From quite general considerations it can be foreseen that the critical field should be given by an expression of the type

$$\mu H_c \approx kT_c$$

whatever the mechanism of interaction may be. One foresees a critical field of the order of hundreds of gauss for the paramagnetic alums (if the ordered state really is antiferromagnetic), thousands of gauss for a substance with a Curie point of a few degrees, and well outside experimental possibilities for most of the antiferromagnetics. The effect probably occurs in quite a number of the paramagnetic alums, but is hard to detect experimentally because it is probably masked by the peculiar hysteresis effects we have just described and also because a change in the magnetic field necessarily implies a change in the temperature of the salt also. The characteristic maxima in the susceptibility associated with an antiferromagnetic transition were, however, detected by Garrett (1951) in cobalt ammonium sulphate, and he was able to map out a critical boundary curve in the *H-T* place in qualitative agreement with theory. Later Gorter *et al.* (1953), working with $CuCl_2.2H_2O$, have shown the existence of the same effect. This substance has an antiferromagnetic Curie point with a well-defined specific heat anomaly at about 4·3°K, and the corresponding "critical field" is of the order

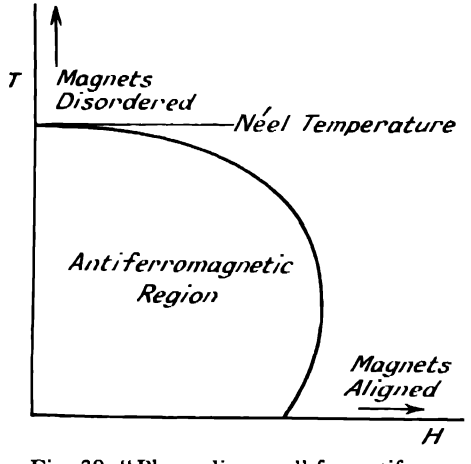

Fig. 39. "Phase diagram" for antiferromagnetics.

of 6500 gauss. The demonstration of the expected effect is complicated by magnetic anisotropy, but its existence is proved both by a very rapid rise in the magnetisation at the critical field, and, even more convincingly, by a characteristic change in the magnetic resonance curves, for details of which see Gorter's paper (1953).

The use of the magnetic resonance technique promises to be an extremely powerful one for detecting antiferromagnetism, see Maxwell and McGuire (1953), who have investigated a number of antiferromagnetic bodies. As one passes through the Curie point, the sharp resonance curve rapidly flattens, and, in the antiferromagnetic region, the absorption is either absent, or has fallen to a small residual value. Theoretically, an absorption at a higher frequency might be expected, but it is only for the $CuCl_2$ case at liquid helium temperatures just referred to that the calculated frequency falls in an experimentally attainable range. Another extremely powerful weapon that has only recently become available for the study of both ferromagnetics and antiferromagnetics is *neutron diffraction*. See, for example, Shull and Wilkinson (1953). This, for the first time, holds out hope of enabling the actual type of alternating structure to be determined, and thus enabling conclusions to be drawn about the interaction responsible for that structure. Thus for MnO, it already seems likely that, as suggested by Anderson (1952), the operative mechanism is the "superexchange" one of Kramers (1934), the lining up of Mn atoms occurring through the interaction of their electrons with those of intervening oxygen atoms. We may confidently expect much further information from this technique, which should provide for antiferromagnetics information quite analogous to that obtainable for alloys from X-ray analysis.

On the theoretical side, a recent development of great interest is the application of the "spin-wave" approach. See Kubo (1953), who also gives a review of the work to date. It might seem that the idea of "spin-reversals" travelling about from atom to atom should apply in principle to the antiferromagnetic case just as easily as to the ferromagnetic one, but the quantum-mechanical specification of the ground state is not so easy, and this leads to certain technical difficulties which are discussed by Anderson (1952) and can probably be overcome. See also Lidiard (1954).

7.7.4. Irreversible Effects in Antiferromagnetics

Various workers have reported complicated magnetic and thermal hysteresis effects but nothing corresponding to the domain theory of ferromagnetics has yet been worked out. The existence of boundaries dividing regions of different types of order, and of "surfaces of mismatch" between two regions with the same type of order seems both possible and likely, but there is nothing corresponding to the parts

played by the magnetic field and magnetic energy in a ferromagnetic. The interplay between exchange energy and anisotropy may very well lead to domain walls of finite thickness, just as we found in the ferromagnetic case. The existence of "surfaces of mismatch" between domains in an alloy with a superlattice can be regarded as certain, and since the disappearance of such a surface would or might require very many atoms to exchange *places* the persistence of such surfaces for long periods of time can be understood (p. 33). It *may* be easier for a "surface of mismatch" or "abrupt domain boundary" to disappear from an antiferromagnetic because the reversal of spin-directions can occur rapidly. However, the boundary *may* resemble a domain wall in a ferromagnetic and, if so, its creation would require a finite energy, and it might persist indefinitely. Kittel (1951) has attempted a theory of domains in paramagnetic alums (nearly pure magnetic interactions) and considers that the domain walls are probably abrupt. No experimental tests of his conclusions seem to have been made yet.

The occurrence of time-effects in the *antiferromagnetic* state hardly seems to have been studied at all. Above the Curie point, where we have a paramagnetic state, relaxation phenomena have been much studied theoretically and experimentally since their discovery by Gorter in 1936, the main processes being the sharing of energy among an assembly of interacting spins (the spin-spin interaction) and the transfer of energy between the spin-stem and the crystal lattice (the spin-lattice interaction). These are quite analogous to the effects studied in ferromagnetics by the resonance techniques. Although these studies raise very many points of great interest, they do not seem to throw any direct light on the problem of changes of state, and we shall not discuss them further.

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CHAPTER VIII

Ferroelectricity and λ-point Anomalies in Solids

8.1. Ferroelectricity

The phenomenon of "ferroelectricity", that is, the occurrence of very large dielectric constants, remanence, non-linear susceptibility and hysteresis in dielectric materials was first discovered in Rochelle salt; Valasek (1921). Since then, the effect has been found in two other classes of compound, one of them typified by potassium hydrogen phosphate (KH_2PO_4), Busch and Scherrer (1935), the other by barium titanate ($BaTiO_3$) (discovered independently by a number of people). For a general account of properties, see von Hippel (1950). [There is also a class of compounds and mixtures, known as *electrets*, which, when polarised by an external electric field in the liquid state, then solidified with the field still applied, retain a polarised state almost indefinitely. The nature of this phenomenon is not known for certain, but it is almost certainly not a phase transition in the accepted sense. For a review of *this* field, see Guttmann (1948).]

In spite of the superficial similarities with ferromagnetism we realise that there are also some very definite differences. In the first place, the strength of the interactions between dipoles (such as water molecules) which ordinarily occur in crystals is, by itself, quite enough to account for Curie temperatures of the observed orders of magnitude of hundreds of degrees Kelvin. In principle, therefore, there is no need to look for other interaction mechanisms, granted only that the dipoles exist. On the other hand, the detailed behaviour of the three types of substance is so different that it is clear that there must also be big differences in the permissible physical models. Rochelle salt and its isomorphs have *two* Curie points, the ferroelectric effects only occurring *between* them. The ferroelectrics of "phosphate" type each have one Curie point, while the "titanate" type may show as many as *three* transitions. In all cases, the transition is accompanied by a recognisable change in crystal structure and, in the Ba titanate, although there is only one "ferroelectric" Curie point, there are three changes in crystal structure. At the Curie point itself (120°C) the symmetry of the crystal changes from the cubic perovskite structure to tetragonal, at about 0°C from tetragonal to orthorhombic, the spontaneous polarisation at the same

time becoming parallel to a face-diagonal instead of a cube edge, while at about −70°C, there is a further change in crystal symmetry from orthorhombic to trigonal, the polarisation now becoming parallel to a body-diagonal instead of to a face-diagonal.

It is clear that we cannot at present hope to do more than obtain very rough theories of the effect in these three typical cases. For the titanates, it is quite clear that the crystal symmetry is intimately related to the spontaneous polarisation, and, since we are not at present in a position to estimate the energies and entropies associated with different crystal structures with sufficient precision to enable us to *predict* structural transitions, it is clear that all that we can hope to do is to find plausible reasons why the perovskite structure should be especially favourable for ferroelectricity to occur. Since the discovery of barium titanate, the effect has been found in quite a number of other crystals of similar structure. (See Kittel, *Solid State Physics* (1953), for a list of such crystals and a survey of the literature.)

8.1.1. Barium Titanate

We also refer to Kittel's book for an exposé of the calculations by Slater (1950) and others. The mechanism invoked may be described as the "polarisation catastrophe" and it is somewhat different from any co-operative effect that we have so far met. Very briefly, it is that the atoms in the crystal can each acquire dipole moments as a result of thermal agitation displacing the positive nuclei relative to the negative electrons. They can also acquire dipole moments as a result of the same displacement due to polarisation by the fields of other dipoles. In addition to this, electrostatic fields can be set up if the ions in the crystal are *shifted bodily* from their equilibrium positions which, again, can happen as the result of thermal agitation or in response to electrostatic fields. For reasons that will be outlined below (p. 230) the latter effect occurs mainly with the titanium ions. If the interactions between the dipoles are sufficiently strong, it can happen that the spontaneously electrified state is the most stable, the electrostatic interactions of the dipoles compensating for the energy that has had to be expended to polarise some of the atoms, and to displace some of the ions, probably the titanium ions, from their equilibrium positions. The next task is to find a reason why the perovskite structure is especially favourable for such behaviour, otherwise there is difficulty in understanding why this phenomenon of spontaneous polarisation does not occur in a great many solids.

At first sight, since we have a cubic structure, it might be thought that the use of the Lorentz field should give a sufficiently good answer for the field available to polarise atoms and ions in a lattice whose total polarisation is P. However, although the lattice as a whole has cubic symmetry

above the Curie temperature, the environment of each oxygen atom is *not* cubically symmetric and the use of the factor $4\pi/3$ is definitely incorrect. Instead, we have to make a calculation on the following lines: We have four types of lattice point, one sublattice occupied by barium atoms, one by titanium atoms and the two others by oxygen atoms. We let P_1, P_2, P_3, P_4 be the mean dipole moments per unit volume associated with these four types of atom. Then the field at each type of lattice point is given by a set of equations:

$$\begin{aligned} E_1&=E_0+q_{1,1}P_1+q_{1,2}P_2+q_{1,3}P_3+q_{1,4}P_4 \\ E_2&=E_0+q_{2,1}P_1+\ldots \\ E_3&=E_0+q_{3,1}P_1+\ldots \\ E_4&=E_0+q_{4,1}P_1+\ldots \end{aligned} \tag{1}$$

E_0 being an external applied field, and the coefficients q_{mn} can be calculated, as they represent the fields due to dipole lattices. See, for example, Luttinger and Tisza (1946; 1947). Now P_n is also related to E_n by the equation

$$P_n=\alpha_n N_n E_n \tag{2}$$

where α_n is the polarisability of the atom of type n ($n=1, 2, 3, 4$) and N_n is the number of such atoms per unit volume. A "ferroelectric catastrophe" occurs when equations (1) and (2) can be satisfied by non-zero values of P_n for $E_0=0$ and the limiting condition for this (which is also the limiting condition that a spontaneously polarised state would have a lower energy than one with zero polarisation) is that the determinant

$$\begin{vmatrix} q_{1,1}-\alpha_1 N_1, & q_{1,2}, \ldots \\ q_{2,1}\cdot & q_{2,2}-\alpha_2 N_2, \ldots \\ \ldots & \ldots \end{vmatrix} \tag{3}$$

should vanish. Inserting numerical values for the polarisabilities and making a reasonable allowance for the contribution to the "effective polarisability" of the titanium ion, due to the fact that it can be *displaced* from its equilibrium position in the lattice as well as becoming polarised electronically, one concludes that the sudden setting in of a polarised state at a certain temperature at which the determinant first vanishes is reasonable. If this theory is correct, we have an instance of a type of transition foreseen as possible by Tisza (1951). See p. 16 for a discussion. For such a transition, the main effect of temperature appears through changes in the polarisabilities α_1, α_2,. . ., the q's and the N's hardly changing with T. As Tisza (1951) points out, such a transition is *not* necessarily associated with any discontinuity or other anomaly in the specific heat, even though the transition sets in quite sharply as the temperature reaches the value at which (3) is first satisfied. One cannot tell *a priori* from (3) whether we get the P_n's gradually growing from

zero, or whether they jump suddenly to finite values. Experiment seems to indicate the latter behaviour for $BaTiO_3$. Evidently, the P_n's will grow to values at which it is no longer a good approximation to treat the coefficients in equations (1) to (3) as linear coefficients independent of the P_n's. We should require knowledge of the non-linear terms, neglected in equation (1), in order to predict the *type* of phase-transition (in the sense of Chapter II) *a priori*. Equations (1) to (3) are, however, enough to locate the *position* of the expected transition.

This abnormal behaviour of the perovskite lattice thus seems to result from a "conspiracy" of two quite distinct factors:

(a) The relation of the size of the titanium atom to the lattice constant is such that it can be displaced an appreciable distance from equilibrium without large restoring forces appearing.

(b) Because of the special arrangement of the oxygen and titanium atoms, some of the coefficients q_{mn} turn out to be numerically about 8 times as great as the value $4\pi/3$ that they would all have if all the ions in the lattice had environments of strictly cubic symmetry while others are negative or nearly zero. This effect arises mainly because the titanium and oxygen atoms are arranged in straight lines (see Kittel, *Solid State Physics* (1953)), and the fact that the hexagonal modification of $BaTiO_3$ is not ferroelectric may possibly be explained in this way.

8.1.2. Rochelle Salt and KH_2PO_4

A theory of Rochelle salt was attempted by Fowler (1935), as an extension of the work discussed later in this chapter (p. 232) on the libration-rotation transitions in solids. The theory of Rochelle salt is handicapped by the fact that the positions of the hydrogen atoms are not known. Actually, the mechanism cannot be that of "pivoted water molecules" that Fowler had in mind, because their dipole moments would correspond to a spontaneous polarisation enormously larger than is observed (28,000 e.s.u. instead of the observed 800 e.s.u.). (If only a small percentage of the molecules "line up", or if a large fraction of them "line up", but are allowed to turn through only a few degrees, these are also things that an acceptable theory has to explain.) Another difficulty is that Fowler assumes a rigid lattice, whereas the piezo-electric effects in Rochelle salt are enormously large. In fact H. Müller (1935; 1940 a, b, c) has shown that the apparent occurrence of *two* Curie points under ordinary conditions is probably the result of the interaction of the spontaneous polarisation mechanism, whatever it is, and the piezo-electric effect. If experiments could be done on a "clamped" crystal, his calculations seem to show that only a single Curie point would occur. This is an instance of the fact pointed out in Chapter

II (p. 17) that the apparent nature of a co-operative phenomenon can be completely changed if the thermodynamic constraints are altered. H. Müller suggests that the appearance of spontaneous polarisation is an "instability" type of transition, resulting mainly from the large piezo-electric effect and the normal variation of the elastic constants with temperature, again an idea somewhat on the lines indicated by Tisza (1951). The mechanism envisaged is this. If the piezo-electric effect is large enough, a deformation of the lattice may occur spontaneously, the interactions between the resulting charges being enough to balance the elastic energy. Again, the fact that the specific heat anomaly is very small is in favour of this type of transition, but the actual degrees of freedom that are responsible for the instability are left unspecified.

The salt KH_2PO_4 shows a large specific heat anomaly, so seems to differ essentially from the other two types. Fowler's "pivoted water molecule" theory is clearly inapplicable. Slater (1941) has proposed a theory based on the properties of *hydrogen bonds*, and a somewhat similar theory has been proposed for both the phosphate and Rochelle salt by Ubbelohde and Woodward (1946). The idea is that, if a hydrogen bond links two oxygen atoms at less than a certain distance apart, the proton has just *one* position of equilibrium half-way between the two atoms, but if the bond exceeds a certain length (2·59 ångströms, Huggins (1936)) there are *two* positions of stable equilibrium and the central position is unstable. Thus, the mechanism giving rise to the dipole moments is thought to be the "stretching of the hydrogen bonds" together with the fact that, once formed, the resulting dipole moments would interact and tend to set up an ordered pattern. It certainly seems likely that the hydrogen atoms are very much concerned with the transition, because the substitution of deuterium for hydrogen has quite a large effect on the properties of Rochelle salt (the upper Curie point being shifted from 42° to 59°C) while attempts to make the same substitution in the phosphate often lead to the formation of crystals of a different symmetry (Ubbelohde (1939)). When prepared, the Curie temperature of the deuterated salt is 213°K as compared with 123°K for KH_2PO_4. A theory of the effect of substituting deuterons for protons in hydrogen bonds is given by Pirenne (1949).

8.2. Domain Effects in Ferroelectrics

The existence of domain effects can be regarded as experimentally established for $BaTiO_3$, which can be grown in single crystals that are fairly transparent. Since the spontaneously polarised form is doubly refracting, it is possible to "see" domain boundaries by examination of the crystal in polarised light. Kay (1948), Forsbergh (1949). (Unfortunately only the boundaries corresponding to "90° walls" in ferromagnetics can be easily "seen" thus, because a complete reversal

of the electrification in a domain would not affect its crystal symmetry.) It is known that domain boundaries can be moved extremely easily by very small stresses or electric fields applied to the crystal, but no theory of such domains has been worked out, nor has any real progress been made in interpreting the hysteresis curves of ferroelectrics, though these are qualitatively very similar to those of ferromagnetics. As with ferromagnetics, we might expect domain effects to result from a balance between several effects, and, indeed, the existence of quite a number of effects that are probably relevant, such as the electrostatic interaction, the numerous piezo-electric and electrostriction effects and the possible appearance of surface charges, is already known for certain.

An estimate of the *inertia* of domain walls (on the provisional basis that they are only a few lattice-distances thick) was made by Kittel (1951 b) and gave reasonable agreement with the frequency dependence of the dielectric constant of $BaTiO_3$. Another recent suggestion by Kittel (1951 a) is the existence of "antiferroelectric" bodies. On the basis of the type of theory that we have outlined above, an "antiferroelectric catastrophe" is, in principle, just as likely as a ferroelectric one. One could consider a large number of possible types of alternating structure, in which, for example, alternate *layers* or *rows* of atoms in the various sublattices are polarised in opposite senses, evaluate the fields at each lattice point by summing over all other points in the lattice, and insert the estimated polarisabilities of each type of ion as before. These fields do *not* necessarily vanish except at lattice points which "see" an environment with complete cubic symmetry. Because of the peculiar form of the field due to a dipole, it is entirely possible for an *alternating* structure to give rise to a field at a typical lattice point quite comparable with that due to a *parallel* structure (see p. 229). There does not seem to be any means of predicting *a priori* which type of structure is the most favourable energetically, indeed Cohen found (1951) for the $BaTiO_3$ lattice that ferroelectric or antiferroelectric states were almost equally likely. In fact, some interaction, over and above that for pure dipoles, seems to be required to explain the occurrence of ferroelectricity, rather than antiferroelectricity in $BaTiO_3$. (For a lattice of *equivalent* dipoles in various cubic arrays, Sauer and Temperley (1940) also concluded that an antiferromagnetic state is a somewhat more likely consequence of *pure* dipole interactions than is a ferromagnetic one.)

8.3. The λ-point Anomaly in Solids

This is the phenomenon of a large specific heat anomaly of typical "co-operative" shape that has been found in quite a number of different solids (fig. 40). The best-known examples are methane, the hydrogen halides and various ammonium salts, but quite a large number of cases

are known. Some solids show two or three such transitions at different temperatures, some of which involve a latent heat, while others are of type B or C in our classification in Chapter II (p. 8). Some of these anomalies are associated with fairly obvious changes in crystal structure, which puts them outside the scope of quantitative theoretical treatments for the present, since we are unable to make accurate estimates of the energy and entropy differences involved in such a change in structure. We shall concern ourselves mainly with those transitions which are apparently *not* associated with any major change in the structure, which leaves us with the problem of identifying the physical change which *is* responsible for the specific heat anomaly.

It is usually found that these anomalies are associated in a characteristic way with similar anomalies in the compressibility and coefficient of expansion. Indeed, attempts were made to fit these transitions into

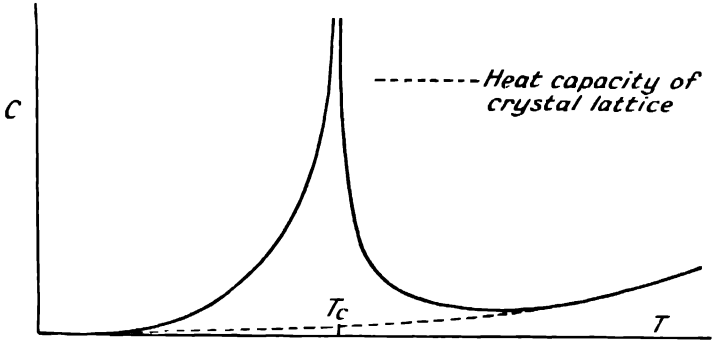

Fig. 40. Typical λ-point anomaly in specific heat.

Ehrenfest's classification, and to fit the data to his equations, the symbol Δ representing a discontinuity

$$\frac{\Delta C_p}{T}=\left(\Delta\left(\frac{\partial v}{\partial T}\right)_P\right)^2\Big/\Delta\left(\frac{\partial v}{\partial P}\right)_T \qquad (4)$$

for a derivation of which see p. 9. However, it is extremely difficult to arrive at an accurate estimate of the "discontinuity" in quantities such as the specific heat, when the anomalies are so "high" and "thin" as are the ones observed. Moreover, some of these transitions show appreciable hysteresis effects. Even if we accept equation (4) as valid for some of the known cases, it still gives us no clue at all to the physical origin of the effect. Lists of solids which show this type of anomaly are given by Smyth (1936), Ruhemann, *Low Temperature Physics* (1937), and Eucken (1939). These reviews also give details of properties that show abrupt changes at the transition temperature, for example the

solid may lose its piezo-electric properties when heated through the transition temperature, or may behave differently towards polarised light, or there may be an anomaly in the dielectric constant. In fact, the search for such properties was guided by the theoretical work of Pauling (1930) and Fowler (1935), whose suggestion was that the phenomenon was a "rotational melting" (this term will be defined in a moment) and might therefore be expected to be associated with some changes in the axial symmetry of the elementary cell of the crystal.

The conception of "rotational melting" can be illustrated by the familiar example of the rigid pendulum. If its kinetic energy is small compared with the potential energy necessary to take it "over the top", its motion is practically *simple harmonic*. If its kinetic energy is large compared with this potential energy, its motion will be a practically *uniform rotation*, moving slightly faster than average when the bob of the pendulum is at its lowest position, slightly slower than average when the bob is at its highest position. Fowler (1935) now introduced the idea that part of the molecule is capable of rotating about some point in the cell, but that it is subject to a "controlling field" which tends to keep it oriented. Since this controlling field would itself depend on the symmetry of the crystal, it would be expected that the effective field in any one particular cell would depend on the state of affairs in neighbouring cells, and that, if one particular molecule acquired enough energy to start rotating instead of oscillating, the controlling field acting on neighbouring molecules would be correspondingly weakened. On this basis, it is possible to derive models giving specific heat anomalies not unlike those observed, though the theory suffers from the usual defect of predicting anomalies that are two "low" and too "fat", but we have already learned not to take such a situation too tragically.

Fowler's (1935) theory, though in principle capable of being considerably refined, contains some undesirable features. The actual entity that is supposed to be "rotating" or "not rotating" is left vague. In a case like methane, the whole molecule is probably involved. Since such a molecule is of fairly high symmetry, the idea of a fairly weak controlling field is reasonable, but, for the ammonium salts, it is not so easy to see what part of the unit cell is supposed to rotate. Another difficulty is that, for the three-dimensional rotator, one has to set up some arbitrary "criterion of rotation". In two dimensions one would say that the pendulum was "rotating" if it possessed enough energy to reach the top, but, in three dimensions, a large variety of modes of motion are possible which, looked at from outside, would appear almost completely symmetrical about any axis, even though the pendulum had not got enough energy to reach the pole. Fowler met this difficulty by introducing a quite arbitrary definition of "not rotating", the pendulum must not possess more than a certain fraction, β, of the energy required

to take it to the pole, and he supposed further that the controlling field was a linear function of the fraction of "not rotating" molecules in the assembly. This assumption is, of course, very similar to that appearing in a Weiss-type theory, whereas the interaction involved is almost certainly of short-range type, mainly between neighbouring cells. Further, the predictions turn out to be sensitive to the precise value of the arbitrary parameter β, which Fowler usually assumed to be $\frac{1}{2}$ to get the best qualitative agreement with experiment. It is, of course, permissible to think of such a parameter as an adjustable constant, but its physical meaning is far from clear.

A second theory of this anomaly was proposed by Frenkel (1935). According to this, the unit cell can exist in two distinguishable configurations of equal energy, and the interaction between neighbouring cells leads to an order-disorder transition essentially similar to these that we have already studied in Chapter VI. (There is, as far as we know, nothing to prevent a particular cell from "flipping over" from one configuration to the other, so that the problem reduces to something resembling the *ferromagnetic* rather than the *order-disorder* model. A model of the latter type would be applicable if the total *numbers* of cells of each configuration were fixed.) We have already discussed the relationships between these two models in Chapter VI (pp. 121–39). A third possibility is that the total numbers of cells are not fixed but that unlike cells like to be together—this corresponding to the antiferromagnetic case. Since the "ferromagnetic" case is the only one which predicts that a given cell will be surrounded by a preponderance of others with the same configuration, it seems the one that is most consistent with the existence of piezo-electric effects in the low temperature modification, and their disappearance at the transition temperature.

Much of the data originally collected by Ruhemann (1937), *Low Temperature Physics*, is consistent with either of these two theories, and it has proved necessary to dig deeper in order to arrive at reasonably certain conclusions. Some confusion has been caused by the claims of certain workers to have "settled" the question in one or more particular cases, when all that they have really done is to show that their experimental result seems to agree with the Frenkel type of theory, but that the Pauling-Fowler type of theory makes no firm prediction about it. Unsatisfactory as such a situation may be, it must regretfully be said that such an experiment "settles" precisely nothing. Among experiments that must be regarded as inconclusive because they cannot lead to a statement of the type "Theory I predicts result A which we observe, while Theory II predicts the different result B . . ." we must put the work on the specific heat anomaly by Lawson (1940) on NH_4Cl and by Stephenson, Blue and Stout (1951) on NH_4Cl and ND_4Cl. The latter authors, after establishing that the entropy change associated

with the transition is $k \log 2$ within the experimental error, take this as "decisive" evidence for an order-disorder type of theory, but it would be quite easy to choose the parameters in the rival theory in order to get a similar result. Lawson (1940), after pointing out correctly that both theories should be compared with C_v rather than with C_p, assembles data which enable him to deduce C_v (C_p actually being measured), and he decides against Fowler's theory because it allegedly predicts an "extra" specific heat of 3 calories/mole associated with the onset of rotation, and the appearance of $3N$ new degrees of freedom while experimentally a value of 6 calories/mole is observed (after making the appropriate deduction for the ordinary lattice specific heat). However, the figure of 3 calories/mole ($3Nk/2$), would mean that the ammonium ions were rotating exactly like *perfectly free gas molecules*, the only contribution to the specific heat coming from the *kinetic* energy associated with the rotational degrees of freedom. The moment we admit that *any* of the controlling field survives above the transition temperature, we have to ascribe a *potential* energy to the rotators as well as a kinetic energy, and each of the $3N$ new (rotational) degrees of freedom must then be assigned a *total* energy of kT as usual. The idea that the controlling field does not vanish, but is only weakened, as we pass through the transition temperature, does not appear explicitly in Fowler's theory, but would certainly be predicted by any more refined version of such a theory which took account of, for example, the finite range of the interactions responsible for the effect. (This could be done on the lines of Bethe's or the other theories that we have reviewed in Chapter VI.) Something of the kind seems to be clearly called for by the fact that the specific heat anomalies have marked high-temperature "tails". Another possibility, explicitly mentioned by Fowler (1935), which we shall refer to again, is that rotations may set in about different axes of symmetry at different temperatures. If only *two* degrees of freedom were involved in an abrupt transition to rotation, we should expect an "excess" specific heat of 4 calories/mole above the transition temperature, a possibility that is certainly not excluded by Lawson's (1940) work. Although his actual *measurements* are of high accuracy, his *final* figures represent the result of subtracting large quantities from one another.

For slightly different reasons we must reject the claim of Alpert (1949) to have "disproved" the Pauling-Fowler mechanism for HCl, HBr, HI, H_2S, H_2Se and (in preliminary experiments) for NH_4Cl. His experiments consist of measuring, as a function of temperature, the "line widths" associated with proton magnetic resonance. In a steady external magnetic field one can obtain resonance between the Larmor precession of the proton magnetic moment and an applied alternating field. If the frequency is held constant and the applied steady field is

slowly varied, one can "sweep through" the resonance curve and measure a "line-width", usually of the order of a few gauss. This quantity depends in a complicated way on a number of different factors, such as the homogeneity of the applied steady field, and the times taken by one of the protons to share its magnetic energy with other protons or to transfer it to the crystal lattice (the "spin-spin" and "spin-lattice" relaxation times). In certain circumstances, explained in the paper, one can be reasonably confident that the observed line width is a measure of two quantities of much more direct interest to us, namely the asymmetry of the magnetic environment in which a typical proton finds itself, and the so-called "flipping time", i.e. the time taken by a typical proton to move to a new position in the lattice, where the magnetic environment is noticeably different. Now the magnetic environment of an average proton depends mainly on the interactions between nuclear moments, which, in turn, depends on the lattice symmetry. This symmetry will not change very much with temperature (unless a completely new lattice structure appears, which event will presumably be associated with a sharp transition temperature). On the other hand, the average environment "seen" by a particular proton is an average over a time interval comparable with the period of the A.C. field. If the proton were part of a system that rotated freely within the lattice its interactions with other nuclear moments should largely average out so that its magnetic environment would be much the same in all parts of the lattice, and the observed line-width should drop to a small fraction of a gauss (this limit being set by inhomogeneities in the lattice and in the applied steady field) in contrast with the line-width of a few gauss calculated on the basis of magnetic interactions between the nuclear moments. Alpert (1949) *did* observe a sudden drop of this very type in the line-width for CH_4 and CH_3D as they passed through the suspected "libration-rotation" transition temperatures. He concluded from this that these transition temperatures *do* probably mark the setting in of practically free rotations. From an *absence* of a similar effect with the other bodies studied (the "line-width" usually decreasing slowly with increasing temperature, some times showing a downward jump of the order of 1 gauss) Alpert also concluded that the corresponding transitions were probably *not* "libration-rotation" transitions.

While Alpert's (1949) conclusion that his results favour rotation for methane and deuteromethane seems sound, his other conclusion that they do *not* favour it for the other bodies seems much more open to question. By a decidedly shaky argument (comparing a "typical solid" with a "typical liquid") he was led to expect a decrease in the "flipping time" by a factor of the order of 10^4 as he passed through a "rotational" transition temperature. In an actual solid, it seems to the author most

unlikely that the time in question could decrease by a factor of more than about 10 on passing through such a transition temperature. This criticism is made for several reasons.

(a) As we have already mentioned, by analogy with the "order in alloys" case, we must expect some "remains" of the controlling field to survive even above the transition temperature, and to disappear only gradually as the temperature is raised further.

(b) Even if we take Fowler's theory quite literally, those versions of the theory that predict a "second-order" (Type B1 in our classification) type of transition, also predict that the parameter S, which measures the "strength" of the controlling field, is *already zero* at the transition temperature itself, the fall in it being continuous and taking place in the region below the transition temperature. Therefore, for such a transition, the "rotation" theory predicts *no discontinuity in the "flipping time" at all* at the transition temperature. For a first-order transition, a discontinuity in S does occur, and it is then reasonable to expect a jump in the "flipping time".

(c) On any theory, it seems most unlikely that any controlling field could, as a result of increasing *thermal agitation*, average itself out so perfectly at all times as to correspond to a change in a time constant by a factor of anything like 10^4 within a range of a few degrees. Such a result would seem to call for a decrease in the controlling field by a factor of the order of 10^6–10^8. For the reasons already mentioned it is pushing Fowler's theory much too far to deduce such a result from it (in spite of the fact that it formally predicts $S \rightarrow 0$).

(d) Alpert's (1949) arguments certainly do not rule out a transition similar to what is now believed to occur in ammonium iodide (rotation about just *one* axis being involved, a possibility that Fowler (1935) explicitly mentioned).

(e) A change in the "flipping time" by a factor of the order of 10 or 20 might be quite obvious in one solid, and yet completely escape detection in another. Alpert's discussion shows clearly that τ_c, the "flipping time", only affects the line width in certain conditions, which are not necessarily satisfied for all the solids concerned.

To sum up, the nature of the transitions in the hydrogen halides still seems to be a completely open question. Tisza (1951) has given some possible interpretations on the basis of his extended classification of phase changes. We pass on to consideration of the ammonium halides, which have been studied by two further methods.

Neutron diffraction has been used on ND_4Cl by Goldschmidt and Hurst (1951), who arrived at a somewhat inconclusive result, finding evidence neither of rotation nor of disorder. The substances ND_4Cl, ND_4Br and ND_4I were studied by the same method by Levy and

Peterson (1952; 1953), who reached the conclusion that rotation was unlikely in the chlorides and bromides, but that one-axis rotation in the iodide was possible. These conclusions seem to be supported by other data. Stephenson, Landers and Cole (1952) concluded from specific-heat measurements that one or more of the rotational degrees of freedom was probably excited in NH_4I. A very careful study of NH_4Cl and NH_4Br was made by infra-red methods by Wagner and Hornig (1950). They concluded that rotational transformations were unlikely because the band characteristic of *torsion* of the ammonium ion was present *above and below* the suspected transitions. A study of NH_4I and ND_4I by Plumb and Hornig (1953) led them to the conclusion that, in these substances, the ammonium ion was probably rotating about one axis only. (The question whether the nature of these transitions would be seriously affected by substituting deuterium for hydrogen was examined by Smits and Tollenaer (1942) and the transitions do not seem to be affected qualitatively).

The "rotation" transition thus seems unlikely for the chlorides and bromides, but is at least possible for the iodides. It appears, therefore, that each substance has to be subjected to an intensive study before any conclusions can be drawn about this puzzling point. The situation about the hydrogen halides, and various other cases such as ammonium nitrate, seems to be left completely open, but it already seems to be quite clear that no simple model will cover a wide sweep of cases as (apparently) will theories of melting and evaporation. (Actually such a conclusion might have been anticipated from the fact that some of these substances have *more* transition points than others that are very similar chemically.)

A review of the earlier data, and of the evidence provided by a study of the dielectric constants and their variations in the region of the suspected transitions, was given by Smyth (1946). While it might seem at first sight that a sudden drop in the dielectric constant as one passes through the transition temperature from above is good evidence that the dipoles are suddenly subjected to an increase in the "controlling field", so that it is less easy for an electric field to orient them, such observations are not completely incompatible with the order-disorder hypothesis. For, if there were two (or more) possible configurations of the unit cell with differing dipole moments, it might well be that the relative numbers of cells in the two configurations could be easily changed *above* the transition temperature by a small applied electric field, while, below the transition temperature, one might expect "domain effects" (Kittel (1951 b)) analogous to those occurring in ferromagnetics. Finite (possibly quite large) electric fields might then be required to produce any appreciable changes is these relative numbers. Smyth (1946), while referring constantly to a "rotational" transi-

tion, is careful to point out that what he has in mind is a transition between two states of affairs, defined as follows: In the low-temperature region the dipoles are practically fixed, in the high-temperature region, the dipoles *either* are completely free to rotate as in Fowler's (1935) crude model *or* to make rapid transitions between different "preferred orientations", a point of view that is approximating closely to that of Frenkel (1935). Thus, once again, it would appear that two apparently "different" theories have far more in common than at first sight appears.

8.4. The Properties of "Long-chain Crystals"

A very interesting field for the testing of theories of co-operative phenomena is provided by "long-chain paraffins" and their derivatives. By this term we mean paraffins with about 20–40 carbon atoms, that is compounds with definite *molecular formulae* and *definite crystal structures*. They occupy an intermediate position between nearly spherical molecules, such as we usually study theoretically, and long-chain polymers, which have no definite molecular weight, and are usually partly amorphous in structure. It has only gradually come to be realised that, at all events in the solid state, these "short-chain"

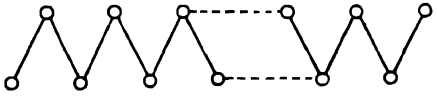

Fig. 41. Assumed form of paraffin-like molecule.

molecules exist in an extended form, in contrast with plastics and rubber-like substances where one has always to consider the possibility of the molecules "curling up". A review of the properties of such molecules has been given by Daniel (1953). Of course, one must not think of the carbon atoms as forming a perfectly straight chain, because two valencies in a 4-valent carbon atom are inclined to one another at the tetrahedral angle (109° 28′), but we are to think of each molecule as a nearly "straight zig-zag" resembling a "Highlander's walking-stick" (fig. 41). In the solid state we may think of the molecules packing in approximately two-dimensional hexagonal fashion, in layers. (Daniel (1953), her figs. 2 and 3.)

When such bodies melt, the molecules apparently still pack like nearly cylindrical rods, but without a regular layer structure, and the evidence is consistent with a square pattern. Such a result is of great interest in connection with the problems of melting and communal entropy (Chapter 5, pp. 70, 103). de Boer (1952) recently suggested that, besides the absence of long-range order, a liquid differed from its solid in having a somewhat lower co-ordination number (9 or 10 instead of 12 corresponding to a close-packed structure). The corresponding

result in two dimensions would be a drop in the co-ordination number from 6 to about 4. Now rods in a two-dimensional hexagonal packing form a structure that cannot be deformed without compressing some of the rods, whereas slight deformations of a square packing (rows of rods being slid along in the manner shown in fig. 42) would be possible with very small changes of energy. Thus, the square packing (even if there are no "holes") can be realised in many practically equivalent ways, which the triangular packing can not, but the calculation of the entropy difference associated with this "looseness" of the square packing is an unsolved problem at present, even in the two-dimensional case. Analogous consequences of a reduction in the co-ordination number must be expected in three dimensions. The relevance of these considerations to the fact that a liquid cannot resist shear while a solid can is also obvious.

A number of other problems, which may be thought of as the two-dimensional counterparts of the corresponding problems that arise with nearly spherical molecules have also been considered. One most interesting point concerns the transition from the monoclinic to the hexagonal form which occurs at about 5°–10°K below the melting point for hydrocarbons of chain length between 20 and 43 carbon atoms. If it be supposed that, as the temperature rises, the molecules acquire more and more rotational energy about their *long* axes (possibly accompanied by some twisting of the chains), the conclusion is that, while at low temperatures, the chains pack in the manner of flat *ribbons*, they will have to be packed in the symmetrical hexagonal arrangement characteristic of *cylinders* when they have acquired sufficient energy of rotation about their long axes, A. Müller (1932). This explanation fits both the X-ray evidence and the calorimetric evidence, for, if turning and twisting occur, large entropy changes are, in principle, to be expected at the transition. The entropy changes deduced from the observed heats of transition are of the order of $k \log 10^4$ per molecule, in contrast with a figure of $k \log 2$ per molecule for an ordinary "order-disorder" transition. The observed figure is, however, quite reasonable for a chain 30 units long, as it would be arrived at if we supposed, for example, that the chains in the low-temperature modification were nearly straight, but that, above the transition there were, on the average, *three* twists in such a chain, each of which twists could be "right handed" or "left handed", leading to a factor of 8, besides which the three places

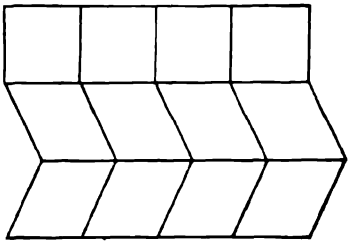

Fig. 42. A possible distortion of a plane square lattice without diminishing interatomic distances or increasing total area.

at which the twists occur in a typical chain can be chosen in about

$$\frac{30.29.28}{1.2.3}$$

different ways. A summary of the experimental data is given by Daniel (1953). Temperley (1956), has arrived at an estimate of the same order for the "configurational entropy" of a hydrocarbon chain by comparing the evidence from various sources. As far as the writer is aware, this is the nearest we have come so far to finding a *theoretical interpretation for an actual thermally induced change of crystal structure.* The theoretical insight that A. Müller's (1932) work gives us is comparable with our present understanding of the order-disorder phenomenon in alloys. In both cases we have a physical model and can *interpret* the effect when it occurs, but we cannot *predict* its occurrence. We do not, for example, know why this transition temperature merges with the ordinary melting point at a chain-length of about 43.

Other, equally interesting, phenomena occur if we pass from paraffins themselves to mono-derivatives, in particular those with a dipole moment, which can act as a "label". The substances that have mainly been studied are halogen derivatives, ketones and esters. The dipole group can act as a "label" in two distinct senses. In the first place, there is the possibility of layers forming in which some of the chains are "upside down" as compared with others in the same layer, and thus we might expect in a pure ketone a set of phenomena analogous to order-disorder effects, or, if we have mixtures of two or more ketones of equal chain-length but differently placed keto-groups, phenomena like those predicted for "regular" solutions (pp. 132–39). Of course, such disordering effects are only possible if the substituted group is not at the centre of the chain. The accompanying phenomena have been studied by Oldham and Ubbelohde (1940), Daniel (1950) and by Crowe, Hoffman and Smyth (1951).

Another possibility that has been explored theoretically is the occurrence of "two-dimensional ferroelectricity", if we suppose that the dipoles are fairly free to rotate by twisting of the chains, their mutual interactions should favour their lining up in some ordered pattern. Such a theory was developed by Frölich (1946) to account for the observation of A. Müller (1937; 1938) that the dielectric constants of such ketones were apparently rising rapidly as the melting point was approached from below, and it seemed a reasonable assumption that the susceptibility was approaching "infinity" in the familiar way but that melting intervened before the transition could occur. However, work with carefully purified preparations by Daniel and Stark (1951; 1952) seems to show that the supposed rise in dielectric constant is spurious and could be produced by ionic impurities present in small amounts.

Yet another question that one asks is whether there is any analogue for the short-chain molecule treated as a *cylinder* of the supposed "vibration-rotation" transitions for nearly spherical molecules, the evidence for which we have discussed above. Hoffman (1951) has used an ingenious model for a paraffin chain with a dipole at one end, such as a bromine derivative. This model supposes that each chain has one position of minimum potential energy, for which the dipoles in neighbouring layers are in a position of minimum potential energy, and a number of Ω of subsidiary minima, these corresponding to the chain being rotated about its long axis (fig. 43) the supposed existence of minima at certain orientations taking account of the fact that the chains are *not* axially symmetrical, and that each is surrounded by six others. It is then possible to define an "order parameter" in terms of the number of chains in the deep minima as compared with the number in subsidiary minima, and to suppose that the energy difference between the deep and subsidiary minimas is itself a function of the degree of

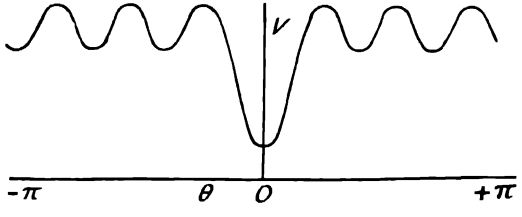

Fig. 43. Hoffman's model.

order. By using an assumption of Bragg-Williams type, and assuming Ω to be of the order of 12, a not unreasonable value, Hoffman (1951) is able to get very fair agreement with experiment, both for the measured entropy of the transitions occurring a little below the melting point, and also with the observed behaviour of the dielectric constant. For an application of an analogous model to long-chain esters, using four positions of equilibrium, see Meakins and Mulley (1953). This makes an interesting comparison with our present ideas about rotational transitions in ordinary solids (p. 232).

Other interesting problems concern the alleged existence of "premelting" in such bodies, and the phenomena which occur when paraffins of *different chain length* are mixed. It is far from clear what exactly is meant by "premelting". Apparently it is an abnormal specific heat beginning *below* the ordinary melting point, which cannot be accounted for by any *known* mechanism, such as an incipient rotational transition, and, *if* it cannot, it is to be considered as an essential precursor

of the fusion process itself. For a survey and bibliography of these two topics, the reader is referred to Daniel's review article (1953).

8.4.1. Long-chain Polymers

If we go from rod-like molecules, about 10–40 units long, to molecules hundreds or thousands of units long, we meet further complications which all stem essentially from the fact that such chains cannot be regarded as straight. If branching of the chains, or extensive cross-linking, can occur, it is not usually possible to liquefy the substance by heating, nor to form a solution by treatment with a solvent (though it may absorb large quantities of liquid to form a gel). If, however, the molecules consist mainly of single chains, the substance will often dissolve completely, and may exhibit almost any type of behaviour on heating, between softening slightly to melting to a fairly mobile liquid. For some types of chain, the segments of neighbouring molecules can form an ordered crystalline structure which can be detected by X-ray methods. However, the crystallisation of a polymer is never *complete*. (If we think of a number of threads stretched in random directions across a frame, it would never be possible to comb them out in such a way that they all lay parallel to one another without an amazing stroke of good fortune. On the other hand any one thread might lie parallel to its neighbours for quite a high proportion of its total length.) The result of this is that, although we have a true phase-transition between an amorphous and a partly crystalline polymer, and, for any given partly crystalline specimen, there will always be a temperature at which the crystalline regions disappear, this temperature usually depends on the "percentage of crystallinity", which, in turn, depends on the previous thermal and mechanical history of the sample. This can lead to quite a variety of hysteresis effects of a kind distinct from anything so far encountered.

We have already discussed the "glass-like" transition (p. 20) and have given reasons for saying that this is not a true phase-transition.

8.5. The Transition of a "Solution" of Tobacco-mosaic Virus

Yet another type of transition could occur in "long-chain crystals" made up of rod-like molecules. In fact, it is quite likely that an analogue of the transition that we are about to describe is identical with the melting of paraffins and similar bodies. The effect that has been detected with tobacco-mosaic virus is as follows: These are probably rod-like molecules existing in an extended form in solution. Above a certain concentration, a solution splits into two distinct phases which can be distinguished in polarised light, one of them being optically anisotropic. Now we can think of two possible types of solution of rod-like molecules.

They might be oriented at random, or they might lie practically parallel. At very low concentrations the random form is to be expected, but, as the concentration increases, the following effect can occur. The molecules tend to align themselves nearly parallel, and thus, for purely geometrical reasons, they are able to pack more closely than is possible for a randomly oriented aggregate. In this way, the loss of entropy that occurs as a result of the alignment may be compensated for by the gain of interaction energy occurring because the molecules are packing more closely.

The interactions between the virus molecules are not known, and may be very complicated in detail. Onsager (1949) has however shown that it is possible to account for the observed transition without making any very specific assumptions about the attractions between the molecules. It is possible to estimate the entropy change associated with the process of alignment simply by making an approximate calculation of the two-molecule distribution function for two molecules in the solution (p. 53), first on the basis that two typical molecules are aligned, secondly on the basis that there is no correlation between their orientations. The mean distance is larger in the latter case simply because configurations in which two neighbouring molecules overlap must be ruled out.

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CHAPTER IX

Superconductivity

9.1. Introductory

The phenomenon of the disappearance of the electrical resistance of mercury was found by Onnes in 1911. He was led to expect, from reasonable extrapolations of resistance-temperature curves, that the resistance would be finite and measurable at the boiling point of liquid helium (4·2°K), but that it would drop smoothly to immeasurably small values within the range of temperatures obtainable by boiling liquid helium under reduced pressure. What, in fact, was found was that the resistance departed abruptly from a smooth curve to drop to an immeasurably small value *within a range of a few hundredths of a degree*. Later experiments have established the existence of this anomalous behaviour for quite a number of metals, and it has also been found that, as experimental conditions approach more closely to those of an "ideal" experiment, the transition becomes progressively more abrupt. Furthermore, under such conditions it seems certain that the resistance is strictly zero, in the sense that the concept has completely ceased to be appropriate, so that we have a transition to a completely new state of matter. It has, for example, been shown that, if there is any residual resistance in a pure superconductor, it does not exceed 10^{-12} of its value just before the transition.

The transition has, therefore, all the hall-marks of a true phase transition, since it occurs at a definite temperature which is characteristic of the substance itself rather than of the particular type of experiment that is used to detect the transition, since the range of the transition can be reduced to a few thousandths of a degree, and since certain physical properties possess measurable numerical values for one phase, but cannot be applied to the other phase at all (just as we can measure the static rigidity of a solid at its melting point, but we can assign no meaning to the concept in an ordinary liquid). Much of the experimental work on the subject has been devoted to looking for properties of superconducting metals that showed similar abrupt changes at the transition point. The discovery of such properties enables one to apply considerations similar to those of Chapter II in order to gain clues about the physical mechanism responsible for the effect. Equally, the discovery of properties that are not changed on passing through the transition temperature has sometimes enabled us

to exclude certain types of mechanism from consideration. For a historical account of the development of our ideas on the subject and a survey of the present experimental position, the reader is referred to Shoenberg, *Superconductivity* (1952), and to F. London, *Superfluids*, Vol. I (1950).

9.2. The Meissner Effect and the Magnetic Field Temperature Transition Curve

In the discussions of Chapter II we have anticipated one of the very important effects that is intimately associated with the transition, namely the fact that the magnetic permeability also drops discontinuously to zero. The application of a magnetic field of a few hundred gauss reduces the transition temperature for all superconductors, and, above a certain applied field H_c, superconductivity becomes impossible at any temperature, the transition curve following an approximately parabolic law

$$H_c(T)=H_c(0)(1-T^2/T_c^2) \qquad (1)$$

where T_c is the transition temperature in zero field. On p. 10 will be found a discussion of the transition of a superconductor based on the experimentally confirmed assumption that the transition is ideally a reversible one, so that a transition curve can be defined in a normal fashion. In Chapter II, we already noticed that this transition was unique in at least two respects—it provides the only known example so far of a transition of type B1, in which the latent heat vanishes at a single point on an otherwise first-order transition curve, secondly, it is the only known case in which the specific heat anomaly is devoid of a "tail" on the high-temperature side. Our general discussions of the relationship between the effective range of the interaction responsible for the transition leads us to conclude, Marcus (1953), that it is of "long-range" type, because, as we have seen (p. 145) any interaction of short-range type almost inevitably leads to a pronounced "tail" in the specific-heat curve.

For a superconductor of reasonable dimensions, we can say that the magnetic behaviour is that of a "perfect diamagnetic", very nearly all the magnetic flux being expelled when the body enters the superconducting state, this usually being described as the Meissner effect. For some superconductors this expulsion of flux is incomplete. For superconducting alloys the latter effect can easily be understood if the composition, and therefore the transition temperature, vary slightly in different places. For, if a specimen is cooled down in a magnetic field, the flux will be expelled from those parts of the specimen with the highest transition temperature and will be concentrated in the regions with lower transition temperature, thus depressing the transition temperature there further. A similar effect is liable to occur with some

of the pure metals, e.g. tantalum, even though precautions are taken to secure purity and uniformity.

A superconducting ring can arrange its distribution of currents in more than one way consistent with the exclusion of an external magnetic field, or it can carry a finite current that persists indefinitely, even though no magnetic field is applied externally. For a discussion of the various possibilities, see Chapter II of Shoenberg's *Superconductivity*. A fuller discussion of the thermodynamics of superconductivity will be found in Chapter III of Shoenberg's book.

9.3. The Penetration of a Magnetic Field into a Superconductor. Surface Effects

The behaviour of the magnetic field near a superconductor is not *quite* the same as that of the electrostatic field near an ordinary metal. A truly static electric field does not penetrate a metal to any reasonable depth, and, as far as we know, the same is true of a superconductor. (For theoretical reasons (F. and H. London, 1935), a small penetration by the electric field *was* looked for by H. London (1936), with a completely negative result.) However, a *magnetic* field does penetrate a distance of the order of 10^{-5} cm even into an ideally pure superconductor, and this results in small specimens having an "effective permeability" that differs from the value of *zero* characteristic of a very large specimen. In addition to this, for a small specimen such as a colloid particle, or a very thin wire or plate, the critical field necessary to destroy superconductivity may increase considerably above the value characteristic of a large specimen. This suggests that "surface tension" effects, analogous to those in a liquid, may occur in a superconducting metal, and may occur for the same sort of reason, namely that the surroundings of a typical electron near the surface of the metal are not precisely like those of an electron deep in the interior. This would require a correction to the free energy of the whole assembly proportional to the *exposed* surface.

There is a certain amount of evidence that *this* particular surface effect is not important. If it were, we should expect an appreciable shift in the *transition temperature* in zero field. Shoenberg (1939; 1940 a) worked with colloidal mercury particles, of sizes of the order of 10^{-4}–10^{-6} cm, and found a transition temperature practically identical with that of bulk mercury, so that the "characteristic length", measuring the ratio of the "surface" to the "volume" contributions to the free energy, cannot be much more than 10^{-7} cm. A result of a similar order of magnitude can be deduced from the following argument: For a body of any shape or size, we have, if we imagine that we start with a purely superconducting state and then increase the field slowly to a value at which the superconductivity is destroyed, the equation

$$\left(\frac{\partial g'}{\partial H}\right)_T = -\int_v I \mathrm{d}v = -Iv \quad \text{if } I \text{ is uniform} \tag{2}$$

where g' is the "magnetic Gibbs function". Integrating up to a field H_c sufficient to destroy superconductivity we have

$$g_n' - g_s' = -\int_v \mathrm{d}v \int_0^{H_c} I \mathrm{d}H_c \tag{3}$$

(We neglect the very small value of I in the normal state.) For a bulk specimen the right-hand side of (3) is simply equal to $+vH_c^2/8\pi$, while for any other kind of specimen, the right-hand side of (3) is simply proportional to the *area under the magnetisation curve*, and the importance of any surface effect will be indicated by the extent to which this area differs from that for a bulk specimen (Pippard (1951 a)) provided only that the magnetisation curve is reversible. (If it is *not* reversible, the true "reversible" curve could still be arrived at roughly by interpolating between magnetisation curves for rising and falling H.) Applying this argument to Shoenberg's colloid results we again deduce a "characteristic length of the order of 10^{-7} cm for mercury. An estimate, of the order of magnitude of 10^{-6} cm, for tin follows from Lock's (1951) measurements of the magnetisation of thin films, but this value is a rougher estimate, as some hysteresis occurred in these measurements. It has sometimes been reported that the zero field transition temperature T_c for films differs significantly from that for bulk metal, but such effects can almost always be traced to stresses in the films or to other spurious effects.

This result most emphatically does *not* mean that the energy associated with a boundary *between* normal and superconducting regions must also be negligible. As we shall see below (p. 271), such boundaries exist in the "intermediate state" of a superconductor, and during its transition, and it is extremely likely that they resemble "domain" walls in a ferromagnetic by being of appreciable thickness. (Such a boundary is analogous to the boundary between a liquid and its vapour, in which it is almost certain that a "shading off", spread over a number of lattice distances, occurs as we travel perpendicular to the phase boundary.) The free-energy difference that we have just been discussing is of a type that has no analogue in the liquid-vapour case. (To realise such an analogue, we should have to compare the free energies associated with a "liquid-vacuum" and a "vapour-vacuum" boundary, neither of which can be realised in practice.) We have also a third possible type of surface effect, which has also no analogue for a liquid, namely the "magnetic Gibbs function" of a specimen with one or more small dimensions is significantly modified by the *penetration* of an applied magnetic field. Contrary to what one might intuitively expect, such pentration makes the superconducting state *more* likely for small

specimens and this *raises* the critical field. (At first sight, this seems inconsistent with the apparent "antagonism" between a magnetic field and the superconducting state, but a little reflection shows that a partial penetration of a superconducting region by a field necessarily *lowers* its free energy as compared with a normal region, where penetration is complete for all thicknesses.) We can examine the situation numerically with the help of equation (2), supposing, for simplicity, that we are working with specimens of simple shape so that I can be treated as uniform. For a normal specimen, we have, by integrating (2) with respect to H,

$$g_n' = \text{constant}$$

(since I is negligible). For a superconducting specimen

$$g_s' = \text{constant} + (vH_c^2/8\pi) - (A\lambda H_c^2/8\pi) \tag{4}$$

where the second term is what we should get if the specimen were perfectly diamagnetic, while the third term is a correction proportional to the exposed area A and is the effective penetration depth λ. (This formula is correct for *any* penetration law, as long as the small dimension of the specimen, v/A, is large compared with λ. For other cases a correction can still be made provided that the detailed penetration law is known.) As we have already seen by considering a large specimen, $g_n' - g_s'$ must be equal to $vH_c^2/8\pi$ so that, for specimens all of whose dimensions are large compared with λ, we predict a limiting law of the type

$$H_e \approx H_c(1 - A\lambda/v)^{-1/2} \approx H_c(1 + A\lambda/2v) \tag{5}$$

for the field required to restore the normal state. This formula is in satisfactory agreement with the results of Appleyard, Bristow, London and Misener (1939) on thick mercury films, and the values of λ so deduced are in general agreement with other methods of measuring this parameter (see Chapter V of Shoenberg's book for a description of such methods). The parameter λ can be said to be known fairly accurately but there is some doubt about whether λ is itself a function of H and about the exact law of penetration. The theory of F. and H. London (1935), that we shall discuss below, predicts the law,

$$\nabla^2 B = B/\lambda^2 \tag{6}$$

The consequences of this law can be worked out exactly for bodies of simple shapes. For a plane lamina, of thickness $2d$ with the origin at the centre, the appropriate solution is

$$B = H_e \frac{\cosh(x/\lambda)}{\cosh(d/\lambda)} \tag{7}$$

where H_e is the field at the surface of the lamina. For $|x| \ll d$, B is very

small, as for a thick superconductor. Since $B=H_e+4\pi I$, we have, by substituting into equation (3),

$$\frac{vH_c^2}{8\pi}=g_n'-g_s'=-A\int_{-d}^{+d}dx\int_0^{H_e}\frac{H_e}{4\pi}\frac{\cosh(x/\lambda)-\cosh(d/\lambda)}{\cosh(d/\lambda)}dH_e \quad (8)$$

or

$$vH_c^2=AH_e^2\{2d-2\lambda\tanh(d/\lambda)\}$$

which is equivalent to (5) when $d\gg\lambda$. Thus, assuming the penetration law (6), we can compute the variation of the critical field for all values of d. The quantity I is the magnetic moment per unit volume and this is equal to

$$I=-\frac{1}{2d}\int_{-d}^{+d}\frac{H_e dx}{4\pi}\frac{\cosh(x/\lambda)-\cosh(d/\lambda)}{\cosh(d/\lambda)}=-\frac{H_e}{4\pi d}\left\{d-\lambda\tanh\left(\frac{d}{\lambda}\right)\right\} \quad (9)$$

and we can thus compute the effective susceptibility of a small specimen as a function of its dimensions. Shoenberg's (1939; 1940) measurements on colloidal mercury extended over spheres of various radii and enabled a check to be made on the analogue of equation (9) for spheres. The agreement with the observed mean susceptibilities of colloid preparations of different mean sizes was only moderate. A fuller discussion on the comparison of the Londons' (1935) suggested penetration law with the experimental material will be found in Shoenberg's book, Chap. V. (He concludes that the suggested penetration law (6) is a satisfactory first approximation, but may be no more than this.)

9.4. The Electromagnetic Equations of a Superconductor

Equation (6) is derived from a set of equations due to the Londons (1935), which replace Ohm's law for a superconductor, and incorporate both the Meissner effect and the apparent absence of resistance within the framework of a single theory, and which make reasonable "order of magnitude" predictions about the penetration depth. The equations give a satisfactory formal picture of the behaviour of a superconductor and have pointed the way to further developments, so that it seems clear that any ultimately successful microscopic theory will have to lead to these equations, or to something very like them, as a consequence.

We make a slight change in our point of view—a formal change only. Up till now, we have regarded a superconductor as a "diamagnetic" body, describing its magnetic state by **B** and **H**, or **B** and **I**. Instead of this, we shall describe it by means of **H**, no longer considered as different from **B**, together with the current density **J**, which is not specified explicitly in the "diamagnetic" picture. The rapid fall in **B**, according to (6), will be interpreted instead as a similar fall in **H**, caused by the presence of "shielding currents" in the thin surface layer. The two points of view, "permeability nearly zero" and "currents keeping the

field out" can be shown to be entirely equivalent, just as we can describe the field of a dielectric *either* by means of "induced surface charges" or "electric moment per unit volume" without changing any observable results.

Let us first examine the consequences of the naïve assumption suggested by the observed "zero" resistance, that some of the electrons (n per unit volume) are completely free to be accelerated by an applied electric field, just as if they were charges in free space. Then $m.\mathrm{dv}/\mathrm{d}t = \epsilon\mathbf{E}$ so that, since $\mathbf{J}=n\epsilon\mathbf{v}$, we have

$$\Lambda\dot{\mathbf{J}}=\mathbf{E} \quad \text{where} \quad \Lambda=m/n\epsilon^2 \tag{10}$$

For the present, Λ is assumed to be constant, independent of coordinates and fields. Taking the curl of both sides of (10), then using

$$\operatorname{curl}\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{H}}{\partial t}$$

we find

$$\operatorname{curl}\Lambda\dot{\mathbf{J}}+\frac{1}{c}\dot{\mathbf{H}}=0 \tag{11}$$

Using

$$\operatorname{curl}\mathbf{H}=\frac{4\pi\mathbf{J}}{c}+\frac{1}{c}\frac{\partial\mathbf{E}}{\partial t}$$

(11) leads to

$$\nabla^2\dot{\mathbf{H}}-\frac{1}{c^2}\frac{\partial^2\dot{\mathbf{H}}}{\partial t^2}=\frac{4\pi}{\Lambda c^2}\dot{\mathbf{H}} \tag{12}$$

Now (12) can be satisfied by the assumption $\mathbf{H}=\mathbf{H}_0$, that is, equation (10) can have the consequence that the field everywhere in the metal is "frozen" at the value it happened to have when the metal last made a transition to the superconducting state. Now $\mathbf{H}_0\neq 0$ contradicts the Meissner effect, so the Londons concluded that equations (11) and (12) were too general and replaced them by

$$\nabla^2\mathbf{H}-\frac{1}{c^2}\frac{\partial^2\mathbf{H}}{\partial t^2}=\frac{\mathbf{H}}{\lambda^2} \quad \text{where} \quad \lambda^2=\frac{\Lambda c^2}{4\pi} \tag{13}$$

$$\operatorname{curl}\Lambda\mathbf{J}+\frac{1}{c}\mathbf{H}=0 \tag{14}$$

which they postulated as the fundamental equations of a superconductor, incorporating the Meissner effect and the "free acceleration of electrons" as consequences. Equation (10) cannot be deduced from equation (14), but by differentiating (14) with respect to t, we can deduce instead $\Lambda\dot{\mathbf{J}}=\mathbf{E}+\operatorname{grad}\phi$. The possibility that grad ϕ differed from zero was examined by F. and H. London (1935) but they finally concluded that it must vanish, otherwise *electric* fields would also penetrate a superconductor to a depth of the order of λ, and the existence of such

an effect was disproved experimentally by H. London (1936). It appears therefore that equations (10) and (14) are suitable for replacing Ohm's law in the description of a superconductor. We get satisfactory agreement with the observed penetration depths if we suppose that $n \approx 10^{-1}-10^{-2}$ "superconducting electrons per atom", which is a not unreasonable assumption.

The Londons have shown further that equations (10) and (14) follow as consequences of the postulate

$$\mathbf{A}+\Lambda c\mathbf{J}=0 \tag{15}$$

which would give as the "equation of motion of a superconducting electron"

$$\mathbf{v}+\epsilon\mathbf{A}/mc=0 \tag{16}$$

where $\mathbf{A}$ is the vector potential so chosen that the scalar potential V vanishes. For the "one-electron" problem in wave-mechanics, the relationships between wave function and charge and current are

$$\rho=\epsilon\psi\bar{\psi}$$
$$\rho\mathbf{v}=(h/4\pi im)(\psi \operatorname{grad}\bar{\psi}-\bar{\psi}\operatorname{grad}\psi)-(\epsilon\mathbf{A}/mc)\psi\bar{\psi} \tag{17}$$

Now we know classically that an assembly of free electrons in a box has no mean magnetic moment when a magnetic field is applied (van

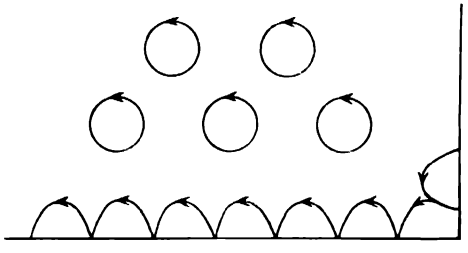

Fig. 44. Absence of diamagnetism in classical model.

Leeuwen's theorem, see van Vleck, *Electric and Magnetic Susceptibilities*, p. 94). This is rather a surprising result, because one expects the electrons to form spiral paths round the lines of force, and thus to give rise to a diamagnetic effect, but, in a classical assembly, the added effect of the small number of electrons near the walls of the vessel will lead to a net magnetic moment of zero (fig. 44). This situation is not very much changed by a passage to quantum theory, except that the balance is now not quite perfect, and we are left with a very feeble diamagnetism, Landau (1930) (the Landau-Peierls diamagnetism). In other words, the application of a magnetic field introduces first-order perturbations into the wave functions, which are such that, for all levels, the terms on the right-hand side of (17) very nearly cancel. Now, if we suppose that there is some coupling between the electrons

that suppresses this first-order perturbation, so that the wave functions are *practically the same* as they were in the absence of a magnetic field, the first term in (17) is still nearly zero even in a magnetic field, and we get equation (16) and can deduce (10) and (14) as consequences. F. London (1948) has, in fact, shown that the *induction of a persistent current in a ring* and the *absence of resistance* when a current is fed into a superconductor from outside can all be deduced as logical consequences of postulate (16).

Fröhlich (1951 a) has pointed out that complete "rigidity" is not a necessity, that is, the terms in brackets in (17) need not vanish *completely*; all that is required is that a term proportional to **A** should survive on the right-hand side of (17) when we insert wave functions that take some account of the coupling mechanism, whatever it may be.

It may seem strange that this postulated "rigidity" of the *wave functions* can have a *large* diamagnetism as a logical consequence, while the opposite assumption that the wave functions "adapt" themselves to an applied field leads to a very small diamagnetism. This is the very opposite of what one intuitively expects, and arises from a confusion between the "classical" concepts ρ and $\rho\mathbf{v}$ and the wave function ψ itself, all of which *describe* the motion of the electrons but do so from different points of view. Equation (17) represents the "code" by which we go over from wave functions to classical conceptions like ρ and $\rho\mathbf{v}$ and applying a magnetic field results in this *code* being changed, as well as in a change in the wave function. According to this picture, electrons in "normal" levels change their wave functions in such a way that their susceptibility remains nearly zero, while electrons in superconducting levels change their wave functions only a little.

While a comparison of equations (16) and (17) is extremely suggestive, it must be emphasised that a model that leads to an equation like (16) is not the only one that can lead to superconductivity. We also have the resource of admitting that the cancellation on the right-hand side of equation (17) is complete as far as first-order terms in **A** or **H** are concerned, but that the Landau-Peierls diamagnetism, which results from corrections to the energy of the second order in **A** or **H**, is greatly in excess of the "free-electron" value. For a free-electron gas it is well known that the diamagnetism is exactly one-third of the spin paramagnetism (the latter effect not being described by Schrödinger's equation because it results from the "lining up" of the electron spins by a magnetic field). This factor 1/3 is peculiar to the "free electron" case, and would not apply, for example, to electrons in a Brillouin zone in a metal, even though such electrons can, for a great many purposes, be considered to behave like free electrons with an "effective mass" m_{eff}, that differs from their true mass. However, the diamagnetic susceptibility varies as $(m_{\text{eff}}/m)^{-2}$ (see Bardeen (1950), footnote 11),

while the spin-paramagnetism is directly proportional to m_{eff}. Thus, by postulating a sufficiently small effective mass, we might expect to get a diamagnetism as large as we please, and this is the basis of Bardeen's explanation of superconductivity (1950). See, however, p. 257 below.

Fröhlich's (1950) and Bardeen's (1950) theories of superconductivity will be discussed below. For the moment, it is sufficient to say that they are both based on the idea of the interaction of the conducting electrons with the sound waves representing the motion of the positive ions according to a Debye-like model, but that they are essentially different theories, because Fröhlich (1951 a) attempts to derive an equation like (16), based on the survival of first-order terms in **H**, which, if it can be proved, predicts as we have seen, many, if not all, of the observed properties of superconductors. Bardeen's explanation is based on the appearance in the energy of second-order terms in **H**, which may, in certain circumstances, become large.

Meanwhile, it seems advisable to point out that Fröhlich's (1951 b) criticism of Bardeen's point of view is itself at least incomplete. Fröhlich points out correctly that the idea of a correction to the energy of the order $II^2/8\pi$ per unit volume, does *not* lead to the same state of affairs as would a constant susceptibility of the order of $-1/4\pi$. However, it seems to the writer that the state of affairs inside such a strongly diamagnetic body cannot possibly be one of *constant* susceptibility, the situation being essentially unlike that inside a paramagnetic body, where there is no *a priori* reason why the susceptibility should not be extremely large and constant. For a nearly perfect diamagnetic, the situation, on the contrary, must be of the type indicated by equation (8) above, in which II is constant through the body, but I and B are varying extremely rapidly as we approach the surface. Thus, the actual value of χ must certainly vary with distance from the surface, though it is impossible to say without a detailed model whether χ is also a function of H. It would be very difficult to discriminate experimentally between a field penetration that was actually approaching *zero* and one that was approaching *a small constant value* as the specimen thickness increased. This remark was made to the author by Bardeen (private communication.)

The situation can also be put in this way. Let us consider a flat plate, and divide it up into layers parallel to the surface. Now the electrons in the outer layer will "see" the field **H** outside, and the vector potential **A** occurring in the usual equation (17) will correspond to this field. However, the electrons in inner layers are strongly shielded by the outer layers, and "see" a smaller field **B**, and *their* wave-equation will contain the corresponding vector potential **A**. (Since **B** is the source-free vector, **B**, and not **H**, must be used in determining **A**.) This means

that **B** can never drop actually to zero, but must always have the same sign as the applied field **H** outside, however far we go into the metal. (This agrees with common sense. If the shielding due to the outer layers were *too great*, **B** would have a nodal plane, and one can reasonably conclude that this would result in a higher energy than if **B** had the same sign everywhere.) Fröhlich (1951) also concluded that, to get a physically sensible result, there must be *some* penetration by the field, however thick a layer may be, and however large the diamagnetic term. The determination of the law of penetration may well involve solving a problem in which the vector potential **A** as well as the wave function ψ are functions of distance, but this is not the same thing as saying that a theory leading to such a problem is *a priori* unacceptable. It is almost certainly *not* possible to set up a consistent picture with a constant χ comparable with $-1/4\pi$ and to this extent we agree with Fröhlich (1951 b). Preliminary calculations on the effect of introducing into the wave equation a vector potential that itself varies strongly with distance from the surface of a metal have been made by Papapetrou (1951), with promising results. See also Klein (1944).

9.5. The "Two-fluid" Model of Superconductivity

So far, we have supposed that the spectacular properties of superconductors are associated with certain electronic states, probably rather few in number. We now consider the remaining electronic states, which we may suppose to be very similar to those of an ordinary metal. While many types of experiment can be carried out in which the "normal" electrons play no rôle, because normal currents are "shorted out" (or decay away because of the finite resistance), there are many other types in which the normal electrons must be considered explicitly. In the first place, any theory of the transition itself obviously requires some description, however rough, of the thermodynamic properties of the "normal" electrons. Secondly, the equilibrium properties of the superconducting metal certainly involve the normal electrons. Thirdly, any attempt at describing the intermediate state, which is almost certainly some intimate mixture of normal and superconducting metal, involves the normal electrons. Fourthly, any alternating current experiment on a superconductor will involve "normal" currents as well as "superconducting" ones.

The simplest assumption that we can make is that the normal and superconducting electrons are capable of carrying currents independently of one another. To explain the existence of a transition temperature, we suppose that the total *number* of electrons of the two kinds is fixed, and that the relative proportions vary with temperature, the number of superconducting electrons becoming zero at the transition temperature. The electric field in a superconductor will both accelerate the super-

current, as in equation (10) and also excite a normal current according to Ohm's law, so that, instead of (10) we have

$$\Lambda \dot{\mathbf{J}}_s = \rho \mathbf{J}_n = \mathbf{E} \tag{18}$$

Clearly, we must also write

$$\text{curl } \mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c}(\mathbf{J}_s + \mathbf{J}_n)$$

since both currents must contribute to the magnetic field H, but there seems to be no reason to modify equation (14)

$$\text{curl } (\Lambda \mathbf{J}_s) + \frac{1}{c}\mathbf{H} = 0 \tag{14}$$

because the equation was derived in order to reproduce the Meissner effect, which is a property of the supercurrent. We can use these three equations in conjunction with curl $\mathbf{E} = -1/c \,.\, \partial \mathbf{H}/\partial t$ in order to eliminate $\mathbf{E}$, $\mathbf{J}_s$ and $\mathbf{J}_n$. We find

$$\nabla^2 \mathbf{H} = \frac{\mathbf{H}}{\lambda^2} + \frac{1}{c^2}\frac{\partial^2 \mathbf{H}}{\partial t^2} + \frac{4\pi}{\rho c^2}\frac{\partial \mathbf{H}}{\partial t} \tag{19}$$

As in the ordinary theory of the penetration of the electromagnetic field into metals, we might expect to be able to "separate out" these terms by working at different frequencies. Inserting reasonable numerical values, the prediction of equation (19) is that the term in $\partial \mathbf{H}/\partial t$ should dominate at infra-red and optical frequencies, so that, in agreement with experiment, there should be no observable difference in the behaviour of the superconducting and normal metals in these regions. In the microwave region, the "eddy-current skin depth" and the penetration depth λ should become comparable. This is also confirmed by experiment, but actually equation (19) has to be generalised. Even for normal metals, it has been found that, at helium temperatures, the mean free path of an electron becomes very long and the normal electrons are behaving like a "Knudsen gas" that is, the main process we have to consider at high frequences is no longer an Ohm's-law type of resistance, due to collisions of electrons with the positive ions, but collisions with the boundaries of the specimen. We refer to Shoenberg's book (Chap. VI) for a survey of the present rather complicated position and for a bibliography. It seems clear that, even after allowing for the uncertainties introduced by the fact that the ordinary theory of the skin effect breaks down, the experimental findings are definitely at variance with the simple idea that the two types of current can simply be added together. We are not neglecting their *interactions* completely by doing this, because their magnetic interaction is automatically taken into account by an equation such as (19).

9.5.1. Gorter and Casimir's Thermodynamic Picture of a Superconductor

This picture is based on the same idea that we can separate the electronic levels into "normal" and "superconducting". If we consider a fixed total number of electrons, we may suppose that a fraction x of them are normal and $1-x$ superconducting. If we assume that they do not interact at all, their total free energy would be the sum of a term proportional to x, and a second term proportional to $1-x$, but this would fail to give a result of the type we want, namely a gradual variation of x with temperature. Instead, we should have a system like a liquid and a vapour, in which, at a fixed pressure, x varies from 0 to 1 without any change of temperature. Gorter and Casimir's picture (1934) assumes a state of affairs in which two types of electron can be distinguished, so that an x can be defined, but they take account of interaction between them by the following assumption for the total free energy of the electrons per unit *volume* of metal:

$$f=-x^{1/2}(\tfrac{1}{2}\alpha T^2)-(1-x)\beta \tag{20}$$

where the form of the function $x^{1/2}$ is chosen empirically to get agreement with experiment. The parabolic temperature law is also empirical, but is suggested, as we shall see, by the form of the observed transition and specific-heat curves. We can now determine the expected properties of this model as follows. For the normal metal, in the absence of a field, we simply put $x=1$, so that we have

$$g'_{\mathrm{n}}=f_{\mathrm{n}}=-\tfrac{1}{2}\alpha T^2 \tag{21}$$

Since M is negligible for a normal metal, and we are neglecting the effect of changes of volume, there is no significant difference between the Helmholtz free energy and the magnetic Gibbs function. Further, since $(\partial g'/\partial H)_T=-M$, (21) will also hold even for a finite field. Since the magnetic moment M is negligible, g'_n will hardly vary at all with H. For a superconductor, in the absence of a field, we have to minimise expression (20) with respect to x, to determine the equilibrium number of superconductivity electrons as a function of temperature. This gives us

$$x=\alpha^2T^4/16\beta^2 \tag{22}$$

so that $f_{\text{electrons}}=-\beta-\alpha^2T^4/16\beta$ and, to get the magnetic Gibbs function for a superconducting metal, we must allow also for the term HI, because a *large* superconductor is not penetrated by a field. (For a *small* specimen, we shall have to allow for the penetration of thin surface layers by a field, in the manner indicated in equations (7) to (9) above.) Thus, for a large specimen $I=-H/4\pi$ and

$$\begin{aligned} g'_s&=-\beta-\alpha^2T^4/16\beta \\ &\quad -H^2/8\pi+H^2/4\pi \end{aligned} \tag{23}$$

where the term $-H^2/8\pi$ arises from the difference in magnetic energy between a superconductor and a normal metal as a result of the fact that the superconductor is not penetrated by H, and the term $H^2/4\pi$ is the term $-HI$ representing the difference between the "ordinary" and "magnetic" Gibbs functions g and g'. It is easy to show that (21) and (22) agree with the observed results for the transition curve and the specific heats. Equating g_n' and g_s' to obtain the transition curve, we get

$$H^2/8\pi=\beta(1-\alpha T^2/4\beta)^2 \qquad (24)$$

which agrees with the parabolic law between H and T already quoted, provided that we identify β with $H_c^2/8\pi$, where H_c is the extrapolated value of the critical field as $T\to 0$, and $4\beta/\alpha=T_c^2$. Differentiating (21) with respect to T, we find that it predicts an entropy and specific heat for the normal metal varying as T, just like the result for the ordinary Fermi gas, while (23) shows us that the entropy and specific heat of a superconductor vary as T^3. These results are in fair agreement with experiment, and, indeed, expression (20) was specially chosen to agree with these results. However, equation (20) states a good deal more than these results we have derived, and we have now to examine whether a result at all resembling (20) can be derived from any theory and whether there are any further consequences of (20) that lead to verifiable predictions.

So far, the only theory that has succeeded in deducing a result at all like (20) is that of Heisenberg (1947) and Koppe (1948), but this theory probably has to be rejected for other reasons. (The more recent theories of Fröhlich (1950) and Bardeen (1950) have not yet been carried to a stage at which they can make firm predictions at finite T.) One can, however, say that a result like (20), in which the electrons are supposed to be in two groups, and yet there is some interaction between them, is reasonable physically. (We recall that, if there were no such interaction, we should have x in place of $x^{1/2}$.) There is, moreover, one consequence of such a model that we have not yet examined, namely expression (22) describing the variation of the "number of superconducting electrons" with T. Combining this with the London theory, the prediction is that the "effective number" of superconducting electrons should vary as $1-x$ or as $1-(T/T_c)^4$, so that λ, the penetration depth, should, according to equation (13), vary like

$$\lambda \propto \{1-(T/T_c)^4\}^{-1/2} \qquad (25)$$

approaching infinity as $T\to T_c$. Such a variation is not at all unlike what is actually found. The reader is referred to Shoenberg's book for a summary of the experimental evidence. Another possible way in which expression (20) might be tested is by using it to compute the transition curves of extremely small specimens after correcting for the penetration

by a field. Actually, the existence of the intermediate state (a mixture of the normal and superconducting states, see pp. 269–75 below) means that it is only under rather special conditions that we get a true superconducting-normal transition for a small specimen. Either we must have an extremely simple geometry, such as a truly tangential field and a specimen in the form of a wire or thin lamina, or the specimen must be so small that it cannot contain more than one domain.

The existence of a parameter corresponding to x in (20) necessarily means that the current can be divided into "normal" and "superconducting" contributions, and we have already pointed out above that it is difficult to reconcile this with all the alternating field evidence. Nevertheless, equations such as (15) and (20) form very useful summaries of large blocks of experimental facts, have been helpful in the past as a guide in the development of theories, and seem likely to remain so for some time.

9.6. Attempts at Fundamental Theories

There have been a large number of attempts to develop theories of superconductivity, and no attempt will be made to discuss them all. Some of them can be rejected out of hand because they give no explanation of the way in which the proposed model is going to give rise to a macroscopic current that can stay constant over long periods of time in the presence of an oscillating crystal lattice. Such a discussion could proceed, for example, along lines indicated in Chapter III (p. 41), or, again, it would be sufficient to show that an equation like (16) followed as a logical consequence of the model. Others seem to arrive at models that are in fundamental conflict with the Bloch theorem which states that the lowest level of an assembly of electrons can carry no current in the absence of a magnetic field even when interactions between electrons are taken into account. (For a proof, see Kittel, Introduction to *Solid State Physics*, Appendix K.) This theorem means that the level in which a superconducting ring is carrying a current is not truly the lowest level of the assembly, and that some explanation of why some metastable level carrying current is possible is always required.

In 1950 the existence of the "isotope effect" was demonstrated in various laboratories, that is to say, it was shown that the transition temperature could be varied by varying the mean mass of atoms in the crystal lattice, the law found being $T_c \propto M^{1/2}$. Since isotopes have exactly the same nuclear charge, and the same arrangement of orbital electrons, the only obvious way in which a change of isotopic mass can affect the conduction electrons is through slight changes in the frequencies of the Debye waves representing the vibrations of the crystal lattice. This provided a further clue to the development of theories.

Any theory that does not take account of this interaction explicitly is faced with the necessity of explaining this relation. In fact, the theories of Fröhlich (1950) and Bardeen (1950) were being developed at about this time, and both of these theories *do* consider this interaction explicitly.

One consequence of this interaction is very well known. It is simply the ordinary electrical resistance of a metal. This is caused by collisions between the conduction electrons and the sound quanta representing the vibrations of the crystal lattice. Put in another way, the conduction electrons forming an ordinary current are "scattered" by the irregularities in the lattice caused by thermal agitation. In the standard calculations of electrical resistance the electrons are treated as "particles in a box", in motion under the influence of a small electric field. The scattering due to sound-waves of a given frequency is computed and summed over all possible frequencies, using Planck's formula to determine the number of sound quanta of each frequency. As is well known, this leads to a resistance proportional to T^5 at low temperatures, the so-called "ideal" resistance, and there is a further contribution due to impurities and other imperfections in the lattice which also lead to scattering of the conduction electrons. Now reference to any standard text on quantum theory shows that there are *two* possible consequences of any perturbation varying with time. It can cause the perturbed system, in this case one of the electrons in the electron gas, to make transitions to new levels. As we saw in Chapter III, it is only processes for which energy is conserved "in the mean" that can lead to dissipative effects (p. 40), and, in perturbation theory, these are the only processes that one ordinarily considers.

A second consequence of any perturbation is that the existing spectrum of energy levels in the perturbed system is *changed.* For a perturbation *not* varying with time this effect is already apparent in first-order perturbation theory, but for an oscillating perturbation without a constant term, such as a sound-wave, this averages out. There is, however, a non-zero effect when one proceeds to second-order perturbation theory. If we use one-electron wave functions, we should find, if we neglected the exclusion principle, the following result for the change in energy of an electron

$$\Delta E = -2 \sum_k \sum_\nu \frac{|M_\nu|^2 f_k}{\epsilon_q - \epsilon_k + h\nu} \tag{26}$$

where f_k is the probability that electronic level k of energy is occupied, and M_ν is the matrix element for the absorption of a quantum of frequency ν by such an electron. However, an expression of this nature assumes the possibility of a transition between the levels ϵ_k and ϵ_q

because it is arrived at by writing the perturbed wave function for the electron originally in level ϵ_k in the form

$$\psi'_k + = \psi_k + \sum_q a_q \psi_q \quad \text{with } |a_q| \text{ small} \tag{27}$$

and this is not permissible if any of the proposed final levels ϵ_q are already occupied. The change in energy of the whole assembly must be obtained by multiplying each term in expression (26) by $1-f_q$, where f_q is the probability of occupation of level q, and summing over all q. That is, to compute the energy change of the whole assembly, we must consider only transitions from an occupied initial level to an empty final level. Thus, although we are not explicitly considering any interaction between the electrons themselves our perturbation theory does lead to an apparent "interaction in k-space" as a result of the exclusion principle.

Thus, this application of perturbation theory does give us an apparent interaction of typical co-operative type in that *the change in the energy of any given electron in the assembly* as a result of the effect of lattice vibrations *depends on the occupation of other levels*. Furthermore, the "interaction" of this type results from the presence of terms like $f_k f_q$ in the energy, and these depend entirely on the momentum of the corresponding electrons and not at all on their positions. Since it is only near the top of the Fermi sphere that f_k and $1-f_q$ are *both* significantly different from zero, it is only electrons near here that can be affected, since the energy of a sound quantum is always small compared with the Fermi energy. Thus, the "apparent interaction" may be described as occurring between electrons of nearly the same momentum, but is of long-range type in ordinary space. Such an interaction may, as we have seen (p. 123), be expected to lead to a specific heat anomaly without any appreciable "high-temperature tail", but a true jump in specific heat as predicted by a Bragg-Williams type of theory. A point very similar to this was made by Marcus (1953).

Bardeen (1950) begins his calculation in very much the same way as Fröhlich (1950) except that he uses initial wave functions that describe both the electrons and the crystal lattice, but he arrives at a preliminary result very similar to the one we have just described. The further development of the work is, however, quite different. Fröhlich (1951 a) tries to show that the perturbed wave functions will possess at any rate some "rigidity" in the sense explained above (p. 254) and thus attempts to derive a result like (16) in the manner already explained. (Presumably this result stands or falls with the validity or otherwise of applying perturbation theory to such a problem.) See below (p. 264). Bardeen (1951 a, b) shows that the perturbed electrons near the Fermi surface may have a very small effective mass, and argues that this means that the "residual" diamagnetism of Landau-Peierls type, may, for

these electrons, be large enough to shut out nearly all the field, consequently, by the argument outlined above, we should then expect to arrive at a penetration depth and a theory similar to London's. This idea may be regarded as a continuation of a line of argument due to Slater (1937). Slater argued that it *might* be a mistake to think that electrons in a metal *always* showed very small diamagnetism because of the fact that they do show it in the two limiting cases of "free-electron gas" (Landau-Peierls diamagnetism) and "tight binding" (diamagnetism similar to that of free atoms, involving changes in orbital radius), simply because diamagnetism is found to be small for *quite different reasons in these two limiting cases*, neither of which reasons would be valid if, for example, the electrons had wave functions extending about 100 lattice distances. (In this connection, the very large diamagnetism of some aromatic compounds, where the wave functions extend over the systems of benzene rings, may be relevant.)

Both Fröhlich's and Bardeen's theories have been the subject of criticisms. We have already noted Fröhlich's (1951 b) criticism of Bardeen's theory and have given reasons for thinking it inconclusive. Fröhlich's theory has been criticised on the ground that perturbation theory is being applied outside its proper limits, Wentzel (1951) having even argued that Fröhlich's supposed criterion for superconductivity would really imply that the crystal lattice is itself becoming unstable. This, and various other criticisms of a similar kind, have been discussed and partly answered by Bardeen (1951 d) in a review article. The existence of the isotope effect, and the considerable success that the ordinary theory of the resistance of metals has had, appears to the writer conclusive evidence that an attempt to improve the perturbation theory is certainly the correct approach. It has very recently been found that bismuth, which "very nearly" satisfies Fröhlich's criterion, can be made superconducting by the application of high pressures, which, apparently, causes a transition in the lattice structure (G. V. Jones (1953)). Various alternative possible approaches to the perturbation problem have been suggested and reviewed by Bardeen (1951 d).

9.7. The Effect of the Coulomb Interaction of the Electrons

Heisenberg (1947; 1948) developed a theory based on the idea that the Fermi distribution of electrons in a metal would be appreciably modified if the Coulomb interaction were taken into account. That this *is* so seems to be conclusively proved by Heisenberg's calculation, which shows that, if we use the "free-electron gas" wave functions and attempt to apply standard perturbation methods, the result "blows up", which is taken to mean that the "free-electron" set of wave functions are too far from the correct ones. He then tries a new set of wave functions, corresponding to modifying the Fermi distribution by adding a "nose"

to the Fermi sphere (fig. 45) corresponding to a finite current and argues that this is a "better" initial set of wave functions, in that the perturbing energy resulting from the Coulomb interaction still diverges but does so "less violently" than before. The theory has been extended further by Koppe (1948), but even in its final form it suffers from the serious defect that, at 0°K, the Fermi distribution should again become spherically symmetrical, which would mean that the London penetration depth would approach *infinity* as $T \to 0$. (Such an effect was, in fact, looked for by Lock (1951) with completely negative results.) In addition, the theory apparently predicts superconductivity for *all* metals (except ferromagnetics), and, since the effect of the lattice vibrations is not considered there is no prospect of predicting the isotope effect. Various other criticisms of Heisenberg and Koppe's theory have been made. For a discussion of them, the reader is referred to Shoenberg's book.

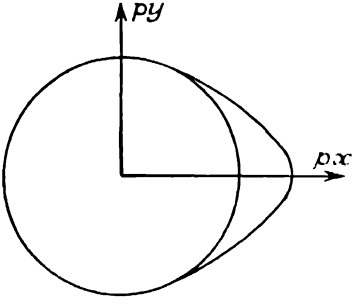

Fig. 45. Modification of Fermi-Dirac distribution according to Heisenberg.

A different theory, also based on the idea of Coulomb interaction, has been proposed by Born and Cheng (1948), but not many details have been published. The main idea is that the effect of the Coulomb interaction is to cause some of the electrons near the top of the Fermi sphere to occupy instead the otherwise empty levels in the "corners" of a Brillouin zone (fig. 46). This effect is also capable of giving rise to a finite current, and has the advantage over Heisenberg's theory that the effect can only be expected to occur in metals where the top of the Fermi distribution is sufficiently near to a zone boundary for the proposed transfer of electrons to be energetically profitable. A criterion on these lines would predict roughly the right metals as superconductors, it would, for example, exclude monovalent metals with top zones only half filled. Moreover, it is possible to avoid the serious obstacle that faces Heisenberg's theory, because of Bloch's theorem (p. 261), for it would be possible to suppose that the state of absolute lowest energy

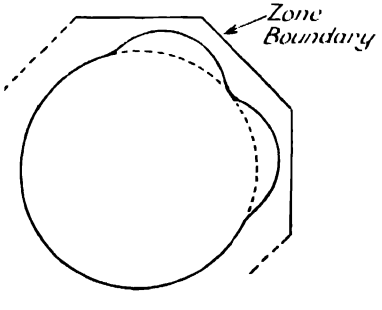

Fig. 46. Modification of Fermi-Dirac distribution according to Born and Cheng.

was one corresponding to "condensation" into two *opposite* corners of a zone, thus corresponding to zero current, but that condensation into a single corner only corresponded to a slightly higher free energy and could thus be metastable.

Neither of these theories seems, so far, to have been developed far enough to show how the Meissner effect can follow as a consequence, nor is it easy to see how either of them can ever predict the isotope effect.

These theories do, however, raise quite an important question. Since the effect of Coulomb interaction is likely to be appreciable, is it legitimate to neglect it, while considering in fine detail the interactions between the electrons and the Debye waves? And, if the Coulomb forces cannot be so neglected, can we justifiably use any of the standard devices for allowing for them partially, such as assuming the electrons to be in a spatially periodic field, due to the positive ions, and then supposing the constants of this field to be chosen so as to allow for part of the effect of the Coulomb interactions? Questions of this kind have been in the minds of metal physicists for a long time, and it is, in some ways, surprising that a "one-electron" model is able to give as good an account as it does of so many of the experimental facts about metals. References to any of the standard books will show that much of the present theory of metals consists of taking a representative electron, using wave-mechanics to compute its behaviour when exposed to various fields, together or separately, and then averaging over all relevant energies and directions of motion. We are led to ask if there is any hope of explaining superconductivity on such lines, or whether we must make some proper effort to take their Coulomb interactions into account, perhaps on lines analogous to the theory of ferromagnetism. A partial answer to this question can now be given.

For a *classical* assembly, we have already found that there is no hope at all of explaining a co-operative effect without taking some *interaction* between the elementary systems explicitly into account. However, this is not true for a quantum mechanical assembly. In the next chapter (p. 303), we shall find that a perfect gas, whose particles obey Bose statistics, would show a transition of typical co-operative type. This difference between classical and quantum assemblies arises from the fact that "classical" particles are regarded as distinguishable and "quantum" particles are not. In a perfect gas, where there are no interactions, the chance that any given particle has of attaining a certain position and velocity are, according to classical statistics, completely independent of the behaviour of all the other particles. If we use either version of quantum statistics, no such result holds, the chance of a particle entering or leaving a certain energy-level *does* depend very much on the number of particles already there. Thus, co-operative effects are,

in principle, possible in a quantum assembly, even if there are no "forces" between the particles.

The result that we have just mentioned for the Bose gas has been of great service in helping us to understand the behaviour of liquid helium, even though the interactions between helium atoms are *not* by any means negligible, and the true behaviour differs very much from that of the ideal Bose gas. The analogous result in superconductivity theory would be that, if we take proper account of the interaction between *independent* electrons and the vibrating crystal lattice, we get an assembly reproducing some of the features of a superconductor, including the transition of co-operative type. It is a result of this kind that the theories of Fröhlich (1950) and Bardeen (1950) are trying to establish, and it would mean that the co-operative nature of the transition arises primarily from the identity and exclusion principles, rather than from the actual interaction forces between the electrons. If such a result can ultimately be established, it will be a very considerable advance, and we should not be surprised to find that the behaviour of the proposed model differed appreciably from that of actual superconductors. Having established this much, it would then be time enough to try and examine the effect of the Coulomb interactions.

9.8. Domain Effects

The domain effects that can occur in a superconductor resemble, in broad outline, those that occur in a ferromagnetic, and have been studied by analogous means. The details are, however, completely different, since, in a superconductor, we are concerned with boundaries between superconducting and normal regions, which are thermodynamically distinct states, while, in a ferromagnetic, the boundaries are between domains that differ only in the *direction* of the spontaneous magnetisation. In spite of the fact that no satisfactory theory of the superconducting state yet exists, it is possible to give reasonable theories of the main observed "domain" effects. It was realised almost from the start that an absolutely sharp transition in a superconductor in the presence of a magnetic field was likely to be obtainable only under ideal conditions. Among other possibilities, if a metal with slight inhomogeneities is cooled in the presence of a magnetic field, one observes apparent hysteresis effects and an incomplete Meissner effect. These anomalies are usually attributed to "locked-in" flux. If some regions of the metal have a slightly higher critical field than others and the whole metal is gradually cooled down, these regions will go into the superconducting state first, and the lines of force will be "pushed out", thus increasing the field in neighbouring regions. If we cool still further, neighbouring superconducting regions may join up, and surround regions that are still normal, because they are still exposed to a field that

is greater than critical. If now we remove the applied field, it does not follow that these normal regions will altogether disappear, because, if a normal thread is completely surrounded by superconducting material, the lines of force passing along the thread may not be able to collapse without passing through superconducting material (fig. 47). Such an

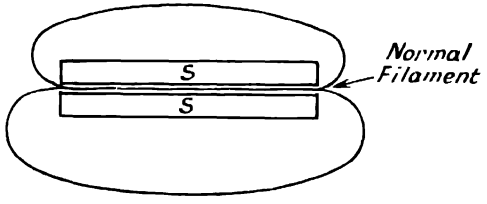

Fig. 47. "Locked-in" flux in an imperfect superconductor.

effect as this is particularly noticeable in alloys. One may get a very large flux frozen in, enough to keep most of the material normal, and yet enough of the material is superconducting to provide resistanceless paths through the material. This state of affairs is sometimes colloquially known as the "Mendelsohn sponge".

We are thus led to think that the coexistence of normal and superconducting regions in one specimen may be quite a common state of affairs, indeed that it is only with a very uniform specimen, such as a wire or cylinder in a strictly tangential field, that one may expect an ideal "all or nothing" transition. One is prompted to ask in what conditions domains can exist in a specimen, and what field distributions can be associated with them. For cases like a long cylinder it is possible to think of a thread of normal metal running along it, the superconducting material contracting around it to just the extent necessary to "compress" the lines of force so that the field reaches just the critical value at the boundary surface. There are, however, more complicated cases in which it seems extremely difficult to find *any* arrangement of domains that is consistent with both magnetostatics and thermodynamics. As an example of such a case, consider a superconducting sphere in a uniform magnetic field that is gradually increased. The sphere will behave as a perfect diamagnetic until the applied field reaches two-thirds of the critical. Elementary magnetostatics then implies that the field has then reached just H_c at the equator (fig. 48). One might expect that a small portion of the sphere near here would become normal, the bulk of the

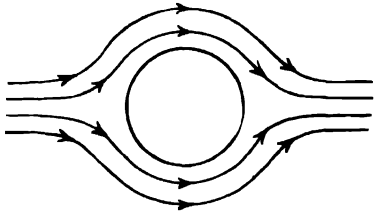

Fig. 48. Field near superconducting sphere.

sphere remaining superconducting, but it proves to be impossible to draw a macroscopic boundary in such a way that the field at all points on it is equal to H_c. Experimentally, it is found that the whole sphere splits up into an intimate mixture of normal and superconducting metal, which behaves magnetically as a material with a nearly uniform permeability lying between zero and unity. Indeed, measurements of its magnetic moment establish that the magnetisation curve is as shown in fig. 49. This state of affairs was described by Peierls (1936) as the "intermediate state". On the assumption that the structure is of fairly fine grain, one can suppose that everywhere inside the sphere, we have, after averaging over domains

$$H=H_c, \qquad B=3H_e-2H_c, \qquad 4\pi I=3(H_e-H_c) \tag{28}$$

where H_e is the external applied field. It can readily be shown, on the basis of elementary magnetostatics, that this state of affairs follows uniquely from the assumptions that $H=H_c$ (which seems necessary if normal and superconductive regions are present together) and that the bulk permeability can be treated as uniform, which follows if the division into normal and superconducting regions is sufficiently fine. Equations (28) are consistent with the picture that every cross-section of the sphere perpendicular to the lines of force will contain the same proportion $(3H_e/H_c-2)$ of normal material, which has a permeability of unity, and carries all the lines of force, the remainder of the cross-section consisting of superconducting material of permeability zero. This situation may be regarded as analogous to that of a vapour and liquid in equilibrium in an enclosure of variable volume. If the volume is altered, the pressure remains constant, but the total volume is proportional to the mass fraction of the assembly in the vapour phase (if we neglect the small volume of the liquid).

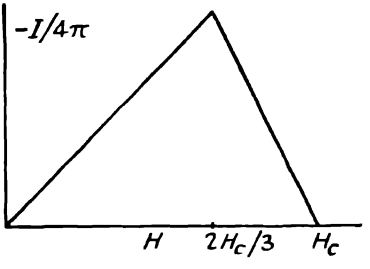

Fig. 49. Magnetisation curve of large superconducting sphere.

From a macroscopic point of view, this description of the intermediate state is quite satisfactory. A magnetisation curve made up of two straight lines, one for $H_e<(2/3)H_c$, corresponding to zero permeability, the other for $(2/3)H_c<H_e<H_c$, corresponding to equation (28), is, in fact, observed experimentally, Shoenberg (1936). To complete the picture, it at first sight seems only necessary to suppose that the normal regions are arranged in some reasonable way, such as laminae or threads parallel to the lines of force, so that the field at the boundaries is always H_c. Such a situation does, however, lead to serious difficulties at the

"ends" of the domains when we come to the surface of the sphere. The type of difficulty that arises can best be understood by reference to fig. 50. The field at a domain boundary must be H_c, and since the field cannot enter the superconductor, it must be tangential at the boundary, so the lines of force must lie in the boundary. Now these lines of force can never be *concave* towards the superconducting region because, if one of them were, the equipotentials perpendicular to it would be

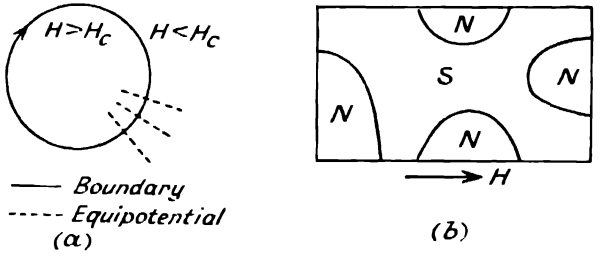

Fig. 50. (*a*) shows that boundaries must be convex to superconducting regions, in which case (*b*) "sharp edges" cannot be avoided.

closer together on the superconducting side than they are on the boundary, and the field in part of the superconducting region would be greater than H_c. On the other hand, if we make our boundaries *always flat or convex* towards the superconducting regions we cannot close them without introducing "sharp corners" somewhere, and again this would lead to fields larger than H_c in part of the superconducting region (or else to fields less than H_c in part of the normal region).

Such a dilemma can be met in various ways. It would be possible to suppose that the domains were so thin that field penetration effects

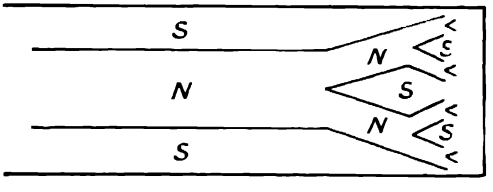

Fig. 51. Landau's branched model.

became important, so that the lines of force do not necessarily have to follow the boundaries of the superconducting-normal regions. As an example of such an assumption, one may mention the "branching domain" model due to Landau (1943). He supposes that the boundaries of the normal regions are everywhere straight, but that, as we approach the surface of the specimen, they progressively split into two, four, eight, ... parts, until, when one is close enough to the surface, the thickness of an individual domain is comparable with the penetration

depth (fig. 51). The optimum geometry of this arrangement is determined by postulating a surface energy analogous to surface tension, and balancing the gain in magnetic energy associated with the branching against the increase of surface energy. Various other models have also been considered, Landau (1937), Andrew (1948), Lifshitz and Sharvin (1951), Kuper (1951; 1954), but none of them is entirely free from objections. One point that *has* emerged is that there are probably a very large number of domain structures that have practically equivalent free energies, so that making such changes as replacing laminae by threads of equivalent cross-section do not greatly change the results, and that magnetisation curves for small specimens (cylindrical wires, thin circular discs) can be made to agree reasonably well with experiment by a suitable choice of the "surface-tension" parameter.

The reader is referred to Chapter IV of Shoenberg's book for a survey of the experimental evidence obtained by Meshkovsky and Shalnikov (1947 a, b; 1949) on the actual domain structure. It is clear that it cannot be described satisfactorily by any simple conception such as laminae or threads, that it probably depends very much on local irregularities in the specimen, and that, even for a large specimen, the structure actually found depends on whether we approach the intermediate state from the all-normal or all-superconducting condition. For small specimens, Desirant and Shoenberg (1948 a), Andrew and Lock (1951), hysteresis effects in the magnetisation curves become very noticeable. This is in agreement with the theoretical result that there are a large number of different microstructures that have practically the same free energy. Nevertheless, the difficulty of finding *any* microstructure that is both magnetically and thermodynamically possible is a tiresome one, not yet satisfactorily solved, which indicates that the theory is incomplete in some respects. It must be noticed that it is *not* possible to avoid the theoretical difficulty by supposing that the domain size is comparable with the penetration depth, because the experiments (which consist of making a magnetic survey of the intermediate state by means of a very small bismuth probe using the magneto-resistance effect) definitely show that the typical domain size is about $10^{-1}-10^{-2}$ cm, and that they remain of such sizes even at the outer surface of a spherical specimen, so that Landau's branching model (1943) cannot be used.

It appears that a solution of the apparent contradiction that results from the domain sizes being large compared with the penetration depth can be obtained if we postulate that the domain boundaries resemble the "walls" in a ferromagnetic material by being of finite thickness. This also enables us to give an interpretation of the postulated surface energy associated with a superconducting-normal boundary. We have already noticed (p. 250) the fact that the difference in surface energies between a superconducting-vacuum boundary and a normal-vacuum

boundary is *not* necessarily comparable with the superconducting-normal surface energy. (In the ferromagnetic case there can be no difference in surface energy between "positive" and "negative" domains exposed to a vacuum, and yet there is a considerable energy associated with a wall *between* "positive" and "negative" domains.) It is customary to express the surface energy of a superconducting-normal boundary in terms of a characteristic length Δ defined in terms of the surface energy proper α_{ns} by the equation

$$H_c^2\Delta/8\pi=\alpha_{ns} \qquad (29)$$

$H_c^2/8\pi$ being the difference in magnetic energy between unit volume of superconducting and normal material. It is found (p. 271) that Δ can be determined, in order of magnitude, by comparing the observed magnetisation curves of small specimens with one or more of the magnetisation curves that have been arrived at theoretically on the basis of various assumed models of the microstructure. (In every case, one concludes that Δ is of the order of 10^{-4}—10^{-5} cm.)

We might expect Δ to depend on the effective thickness of a domain "wall", just like the energy of a "wall" in a ferromagnetic. In the absence of a detailed theory of superconductivity, we cannot expect to make as much progress as has been made in the theory of ferromagnetic domains, but some definite steps forward have been made. From various arguments Pippard (1950; 1951) has been led to postulate the existence of a characteristic "range of order" in a superconductor. That is to say, he supposes that such parameters as the n in the London theory, or the x in the Gorter-Casimir picture, which measure the "mean number of superconducting electrons", can only change significantly over a finite distance which we call the range of order. (In a ferromagnetic, as we saw above (p. 208) the direction of the magnetisation could only *change* significantly over a finite distance, the "wall-thickness", but this does not forbid the *existence* of ferromagnetism in particles that are of significantly smaller dimensions.) The "range of order" has been estimated in a number of distinct ways:

(a) There is a small, but measurable, change in the penetration depth λ with an increasing field. For details of the argument the reader is referred to Section 6.3.5 of Shoenberg's book, or to Pippard's original papers (1950; 1951).

(b) From the sharpness of the disappearance of resistance at the transition temperature. One may suppose that domains of superconducting phase cannot be created by fluctuations unless at least one of their dimensions exceeds the range of order. In this way one can estimate the fraction of material that is superconducting at temperatures near to T_c, Pippard (1950).

(c) Bardeen (1951 b) has pointed out that a concept of this kind is a

necessary consequence of postulating that the superconducting electrons have small effective mass. For, by the uncertainty principle, na^3 such electrons localised within a volume of dimensions a have an energy of the order of $na^3.h^2/m^*a^2$, where n is the number of superconducting electrons per unit volume and m^* is their effective mass. This energy cannot possibly be larger than the gain in macroscopic free energy associated with the appearance of the Meissner effect in a body of

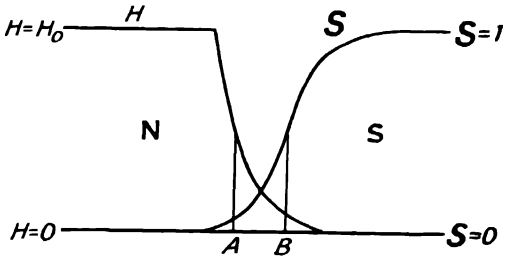

Fig. 52. Pippard's picture of an actual domain boundary. H=Magnetic fields, S=Order parameter.

size a^3, of the order of $H_c^2a^2/8\pi$, and we thus arrive at a lower limit for a.

All of these estimates are consistent with a "range of order", a, in the region of 10^{-4} cm. We might expect Δ, the surface energy parameter, to be related to the range of order a somewhat in the way indicated in fig. 52, which is supposed to represent plots on the same diagram of the "degree of order" S (which is zero for normal metal, unity for superconducting metal) and of the penetration of the magnetic field H, into the boundary region. Let B represent the plane on which the degree of order=$\frac{1}{2}$ and let the field H be considered as effectively penetrating into the boundary region as far as the plane A, the field beginning to fall off at the plane at which the order starts to rise. If we had an *abrupt* rise in S we might expect (fig. 53) the field to penetrate the superconducting region to an effective depth, and the total magnetic Gibbs function would be g_n' per unit volume for everything to the left of B plus $g_s'+H_c^2/8\pi$ per unit volume for everything to the right of B *less* the small correction, $\lambda H_c^2/8\pi$ per unit area of boundary, to allow for the field penetration. In the situation shown in fig. 52 the total magnetic Gibbs function would be g_n' per unit volume for everything to the left of B, $g_s'+H_c^2/8\pi$ for everything to the right

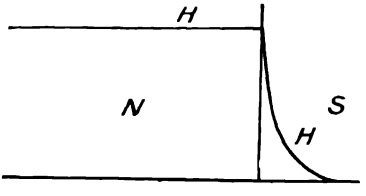

Fig. 53. Conditions at an *abrupt* boundary.

of B, plus a term $AB.H_c^2/8\pi$ to allow for the fact that the field is effectively excluded from the region AB. Thus the extra energy associated with the boundary is $(AB+\lambda)H_c^2/8\pi$, and Δ is thus comparable with, though perhaps somewhat smaller than, the "range of order".

As in the ferromagnetic problem, we must suppose that, if AB were decreased, the fall in the magnetic Gibbs function that would result from the field being admitted to more of the metal, would be balanced by a rise for some other reason. (Bardeen has, as we have just seen, suggested such a possible reason (1951 b).) If so, the actual values of AB and Δ are determined by the condition that the total free energy associated with a boundary is a minimum, just as the width of the wall in ferromagnetic is determined by similar compromises (p. 209).

The existence of fairly thick domain walls is in reasonable agreement with existing evidence. In addition it seems to provide a way out of the difficulties that we have already noticed, of finding a magnetically possible domain structure. For, with such a situation as that shown in fig. 52, the field probably still has to have the *value* H_c at the boundary, but there is no longer any reason to suppose that it *must* be tangential to this boundary, and thus the theoretical objection to boundaries concave to the superconducting region seems to be removed.

9.8.1. Disturbance of Superconductivity by a Current

A curious question arises if we think of what is likely to happen if the magnetic field that destroys superconductivity in a wire is provided by a current. According to Silsbee's hypothesis (1916), resistance first reappears when the current is such as to give the critical field at the surface of the wire, but the resistance is not all restored immediately, and it is of interest to ask what is the state of the wire in the transition region. The central core of the wire cannot be all superconducting, for, if it were, the entire current would immediately flow in it and would give rise to a field at the surface of the core of $2I/r$ where r is its radius. Since r is necessarily less than a, the radius of the wire, and since we are supposing $2I/a > H_c$ this situation is obviously impossible. Equally clearly, the inner core cannot be all normal, for, if the current were spread uniformly over the core, the field at the very centre would be zero. One must thus conclude that the core is in the intermediate state and an arrangement that is magnetically possible, and whose consequences

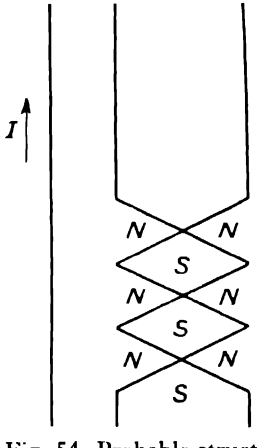

Fig. 54. Probable structure of superconductor carrying a current and in the intermediate state.

give transition curves that are in reasonable agreement with experiment has been suggested by London (1937), the suggested structure of the core being as shown in fig. 54. The question of how to take account of surface effects in this model has been studied by Kuper (unpublished), but no detailed theory has been given. Kuper (private communication) has also investigated the possibility that the domain boundaries may be *moving with the current*. Intuitive arguments lead one to think that stationary domains are rather more probable, but quite a number of results that, at first sight, "seem wrong" have been ultimately accepted in physics. In this particular field, our experience tells us to be particularly cautious about intuitive arguments.

9.8.2. Motion of Domain Boundaries

The structure of the intermediate state as determined experimentally suggests, though it does not actually prove, that under "ordinary" conditions nuclei of one phase are formed at a very large number of points simultaneously, afterwards expanding until they come into proximity with other domains. This is what probably occurs in an ordinary ferromagnetic material, and, as we have seen, it is only under special conditions that we can get domains of macroscopic size, and watch the motion of a single domain boundary. A similar situation occurs if we superheat a liquid, under "clean" conditions we can get very considerable superheating, followed by "bumping", i.e. the rapid expansion of a few large bubbles of vapour, whereas under "dirty" conditions only very little superheating is possible, and bubbles form at many places simultaneously.

Faber (1952; 1953) has performed experiments analogous to the Sixtus and Tonks experiment on ferromagnetic wires (p. 213). It had been known for some time, Shoenberg (1940 b), that in very pure specimens, considerable hysteresis is possible in the sense that the field on a specimen in the normal state can often be reduced very considerably below H_c before it reverts to the superconducting state. Working with a tin rod Faber (1952) found that growth of the superconducting phase starts from "weak spots" on the surface which can act as superconducting nuclei and the growth of superconducting regions from them can be followed by placing search coils in suitable positions along the rod, exactly as in the Sixtus and Tonks type of experiment. The mechanism of growth of the nucleus is however different from the ferromagnetic case, the superconducting domain first extending rapidly along the length of the rod, accompanied by a less rapid lateral expansion and a final stage in which the flux is expelled from the interior. The speed of all these processes is consistent with the idea that eddy-currents, associated with the expulsion of flux from the newly formed superconducting regions, are the main factor limiting the speed of travel

of the boundaries, just as in the Sixtus and Tonks experiments. The properties of the nuclei turn out to be extremely sensitive to the surface conditions, and are completely changed by quite gentle handling. Faber suggests that they represent regions where the "surface-tension" parameter Δ is locally modified by stresses. As is well known, with a positive surface tension, a domain can, theoretically, not begin at all, however great the departure from the equilibrium may be. Faber suggests that local stresses may make Δ zero or negative for the nucleus, and, by making reasonable assumptions on these lines, he is able to account for the variation of ϕ the "degree of supercooling" ($\phi = 1 - (H/H_c)^2$, H being the field at which the domain begins to expand) with temperature. It is possible to work with different nuclei on the same rod by "protecting" the "weakest" ones by maintaining the field near them at values always greater than H_c, at the same time reducing it near other nuclei.

Faber (1953) has carried out a second type of experiment in which a previously superconducting material is suddenly subjected to a field greater than critical. Here, the process seems to be an almost cylindrically symmetrical collapse inwards of the domain boundary. Again the main limiting factor seems to be eddy currents (surface tension now having little influence), but there is evidence that other factors are also concerned in determining the rate for this process.

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CHAPTER X

The Transition of Liquid Helium

10.1. Introductory

Helium differs in several respects from all other substances. It has the lowest boiling point of all gases, at atmospheric pressure it apparently remains liquid however close we approach to absolute zero, and the liquid itself undergoes a transition at 2·18°K of typical co-operative type, the specific heat anomaly being of the characteristic "λ" shape (fig. 40). The P-T diagram is sketched in fig. 55, from which it will be seen that the solid state is not realisable at any temperature unless a pressure of 25 atmospheres or more is applied. For an account of the experimental observations up to 1941, the reader is referred to Keesom's *Helium* (1941), while reviews of the theoretical work have been given by F. London, *Superfluids*, Vol. II (1955), and by Dingle (1952). Apart from the fact that it begins at a finite pressure, the solidification curve seems to be very like that of an "ordinary" substance, Dugdale and Simon (1953). The vapour-pressure curve also shows nothing particularly unusual, and ends suddenly at a critical point in the usual way. Attention has been mainly concentrated on the liquid-liquid transition, and on the remarkable properties of the low-temperature form of the liquid.

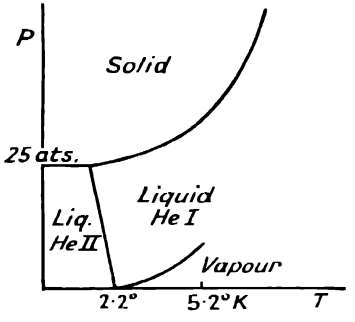

Fig. 55. Diagram of state of helium.

These properties recall in some ways the properties of a superconductor, and they have attracted much attention, not only because of their intrinsic interest, but also because a preliminary theory of them seems to be a vital prerequisite to a proper understanding of ordinary liquids. We make this assertion for the following reason. It is known that the interaction between two helium atoms is of the typical attractive-repulsive type (fig. 56), and that the interactions between other atoms and molecules can be represented, at least approximately, by functions of this kind. Now, unless we have a fairly clear idea of *why* an interaction of the particular strength and range appropriate to helium atoms

is associated with a liquid state with such very strange properties, it must be said that something is missing from the theory of any other liquid, in that we are unable to explain why other liquids do not also show such properties.

Various theoretical calculations of the interaction between two helium atoms have been made, e.g. Slater and Kirkwood (1931), and the interaction can also be estimated by comparison of calculated and observed second virial coefficients, see, for example, Fowler and Guggenheim, *Statistical Thermodynamics*, Chap. VII, but a rather troublesome technical difficulty arises with this second method. For a completely classical assembly, the second virial coefficient is uniquely determined at all temperatures if we *assume* a given interaction function. However, for helium, "quantum corrections" are already becoming significant when the density is large enough for reliable determinations of the second virial coefficient to be made. These corrections to the purely classical theory themselves depend rather critically, see Wigner (1932), on the exact strength of the interaction, in particular on whether this interaction is strong enough to give rise to a bound quantum-mechanical level for two atoms. It is clear that the actual interaction is very *near* this borderline, but it is not quite clear on which *side* of the borderline it lies. The theoretical *a priori* calculations of the interaction are not accurate enough to settle this point definitely, while arguments based on the second virial coefficient are inconclusive for the reason stated. Later on, we shall bring up evidence indicating that at least some of the strange properties of liquid helium can be traced to the fact that the interaction *is near* this borderline.

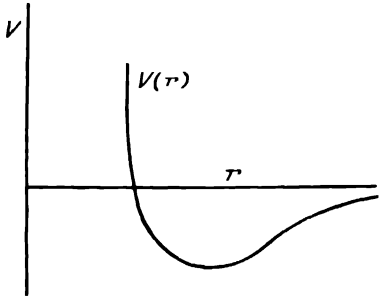

Fig. 56. Assumed interaction function for helium atoms.

10.2. Early Experiments

So far, the only unusual properties that we have mentioned are that the liquid state can persist down to absolute zero and that a transition occurs in the liquid. Since one is accustomed to thinking of a liquid as having a disordered structure, it is natural to ask whether its entropy vanishes at absolute zero. All the available evidence suggests that it does, for example $(\partial P/\partial T)_v$ for the solidification and vapour-pressure curves are both rapidly approaching zero as $T \to 0$, which indicates that the entropies of all three phases, solid, liquid, and vapour, are approaching equality. However, there is no obvious change in the X-ray scattering

as one passes through the transition point (Reekie and Hutchison (1953)). (Because of the uncertainty principle, a disordered *spatial* structure is *not* inconsistent with zero entropy at $T=0$. The liquid-liquid transition has been very carefully studied. At first sight, the only thing that is particularly unusual about it is that dP/dT is negative. Normally, the effect of compressing an assembly is to increase the spacing of its energy-levels, and we might expect a transition temperature to increase also, since our usual criteria for a transition point involve the ratio of kT_c and some typical energy difference. However, the negative slope of the transition curve is not unique—the melting curve of water being a case in point. For an account of the earlier work the reader is referred to W. H. Keesom's *Helium*. It seems to be clearly established that the transition takes place without any measurable latent heat over almost the entire range of the transition curve. (This does not seem to have been actually verified for the region in the immediate neighbourhood of the solidification curve (fig. 55), but is likely to be correct for the entire range.) What is less certain is the actual form of the specific-heat anomaly. For a long time, this transition was thought to be the typical example of a second-order phase transition of Ehrenfest's type (Type B 1 in our classification (p. 9)), and many attempts were made to relate the discontinuity in specific heat to the discontinuities in compressibility and coefficient of expansion (equation (9), p. 10). However, the notion that we actually have an "infinity" in the specific heat, and in one or both of these other coefficients, is equally consistent with the data, Atkins and Chase (1951), Atkins (1953). These workers find that the variations of the velocity of sound, and of the coefficient of expansion become progressively steeper as the transition temperature is approached, in a way that would make it impossible to assign numerical values to any discontinuities that may exist. In this respect, this transition resembles the λ-transitions in solids that we have already discussed in Chapter VIII.

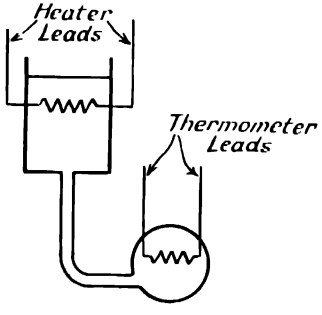

Fig. 57. Measurement of apparent heat conductivity in a liquid.

The λ-transition occurs at the temperature at which bubbling in the liquid suddenly ceases, boiling of the liquid at lower temperatures occurring entirely by evaporation from the surface. This difference in behaviour between the two forms of the liquid was eventually traced to what appeared to be an enormously high heat conductivity. Attempts to measure the heat conductivity by conventional methods, measuring

the rate of transport of heat along a tube by means of apparatus such as that shown in fig. 57, gave results corresponding to extraordinarily high apparent heat conductivities, but the rate of heat transfer depended non-linearly on the temperature-difference, being approximately proportional to $(\Delta T)^{1/3}$ for large temperature differences.

Attempts to measure the viscosity of liquid helium II led to results almost equally remarkable. See, for example, Allen and Misener (1939). Here again, it was never possible to obtain flow of the classical (Poiseuille) type, as the rate of flow through a capillary was never exactly proportional to the pressure-difference across the ends of the tube. Moreover, for long thin tubes, the rate of flow, for a given pressure difference, became almost *independent of the length of the tube*, and attempts to calculate an "effective viscosity" from some of these experiments led to fantastically low *apparent* values, of the order of 10^{-12} poise (as compared with measured values of the order of 5×10^{-5} poise for helium I just above the transition point, and 10^{-2} poise for water at ordinary temperatures). Here again, there seemed to be evidence of some sort of "super-flow", akin to the persistent currents in super-conductors, and it was soon suspected that the abnormally high apparent heat conductivity might be another manifestation of the same effect. Further experiments showed that, the narrower the channel, the more noticeably does He II differ from any ordinary liquid. For example, it is well known to experimenters that a defectively soldered joint, a "λ-leak", may be quite tight for He I and the gas, but passes He II with great ease. It was also found that "pads" formed of compressed jeweller's rouge, which contain tortuous channels of dimensions of the order of 10^{-6} cm and offer a considerable barrier to the flow of all ordinary liquids and gases, offer almost *no* obstacle at all to the flow of He II.

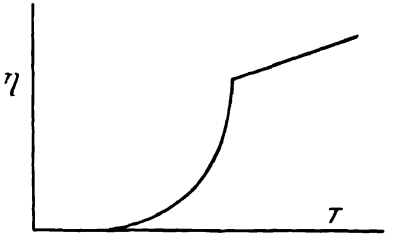

Fig. 58. Measurements of apparent viscosity of liquid helium (Keesom and MacWood).

There are, however, other ways of measuring the viscosity of a liquid. The experiment was tried of suspending a disc horizontally in its own plane by means of a torsion fibre, setting it into oscillation and measuring the rate at which the amplitude decays. The theory of this experiment is complicated but well known, and it was found that, provided that the amplitude does not exceed reasonable values, liquid helium II behaves *just like a classical liquid as far as this experiment is concerned.* The viscosity deduced from such experiments is comparable with that observed for He I. See, for example, Keesom and MacWood (1938).

Fig. 58 gives a sketch of the type of result found. An experiment of this kind is capable of being further developed. In any "oscillation" experiment it is always possible to make observations of two quite independent types. One may measure the *decrement* of the oscillations, or one may measure the effect on the *period*, and both of these effects are expected to be finite for a disc oscillating in a liquid. The increase of the decrement (over and above the value that one gets if the disc is swinging in a vacuum) is to be attributed to the shearing of the layers of liquid in the immediate neighbourhood of the disc. An increase in the period is also to be expected, because the layers of liquid in the immediate neighbourhood of the disc are being "dragged round" by it, and so are contributing to the moment of inertia of the moving system. Calculation soon showed that this second effect would be too small to measure for a single disc, but could be enhanced by working with an oscillating member consisting of a *pile* of parallel discs suitably spaced (fig. 59), Andronikashvili (1946; 1948), Hollis-Hallet (1950; 1952). The effect on the period now becomes large enough to measure, and, although the hydrodynamical problem becomes extremely complicated, it can be solved sufficiently accurately for all practical purposes.

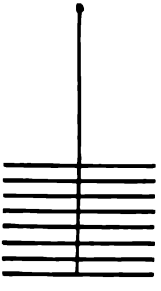

Fig. 59. Oscillating pile of discs for viscosity and density measurements.

It might be thought that such an experiment would give nothing more than two independent measurements of the viscosity. In reality, however, both the damping and change in period depend on both the viscosity and the density of the liquid, and these two quantities involve the viscosity and density in different ways, so that these two types of result give us two equations for the density and viscosity at each temperature. Now the surprising fact is that the observed figures for He II cannot be reconciled with the actual density of the liquid. In fact, they are just what we should get if the discs were oscillating in a liquid of a finite viscosity but of a smaller density than that of the actual liquid, and the ratio (calculated density/actual density) turns out to be a function of the temperature only, and to be independent of the period of oscillation and of the dimensions and spacings of the discs, that is, *this ratio seems to be some property of the liquid itself*. The results of the capillary flow and the oscillating disc methods of measuring the viscosity can be reconciled by the following hypothesis, which seems extremely strange and artificial, but *has* to be taken seriously because, as we shall see below, it is capable of correlating a very large number of other experiments that have been carried out at various times.

10.3. The "Two-fluid" Hypothesis and its Consequences

We assume that liquid helium can be considered *formally* to be a mixture, or solution, of two different liquids, one of which is thought to behave like an ordinary liquid and to have a finite and measurable viscosity, while the other is thought to be devoid of viscosity, and to be capable of slipping over solid surfaces without friction. These assumptions may seem to be completely artificial when applied to something so simple chemically as liquid helium, but we postpone discussion of this point to a later stage. Meanwhile, we trace out their consequences, in the full realisation that they *are* provisional. The attempts to measure viscosity can now be seen in a somewhat different light. If we attempt to measure viscosity by the Poiseuille method, and we use an extremely narrow capillary, the resulting motion will be almost entirely of "superfluid", which we are supposing to be capable of slipping over solid boundaries, while motion of the "normal fluid" will be almost entirely prevented by viscosity. On the other hand, the oscillating disc will drag normal fluid round with it, but *leave the superfluid stationary.* Thus, in one type of experiment we are measuring the vanishingly small, perhaps zero, viscosity of the superfluid, in the other, the presence of the superfluid should not affect the motion of the discs at all, so that in the oscillating-disc type of experiment we are really measuring the viscosity and "effective density" of the normal fluid.

10.3.1. The "Fountain" Effect

So far, the two-fluid hypothesis appears to be a rather far-fetched explanation of the viscosity measurements, but let us accept it quite literally, and see what fresh consequences it would lead to. Already it is clear from the viscosity measurements that the ratio (effective density/actual density) is a measured physical property of the liquid, though the proposed interpretation of it *may* not be correct. Now this ratio of densities, which we may write ρ_n/ρ, is found to vary rapidly with temperature, and at 1°K has already fallen to about 1 per cent (from being unity at the transition temperature). Now a solution of any kind has osmotic pressure, irrespective of whether or not the solute molecules interact with one another. Since the ratio ρ_n/ρ varies with temperature, and since we are capable of making channels, such as the passages between particles of jeweller's rouge, *that can be quickly penetrated by "superfluid" but hardly at all by "normal fluid"*, it is practicable to carry out an experiment analogous to an *osmotic pressure* measurement. Let us suppose that we have two vessels connected only by narrow channels (fig. 60). Now, if there is a temperature difference between the two ends of a narrow channel, the concentration of superfluid will be smaller on the hotter side, and we may expect superfluid to travel

through the channel until a pressure-difference is built up. This phenomenon is in fact observed (though it was actually discovered by accident rather than as a result of any train of reasoning of this sort, Allen and Jones (1938)), and is exactly analogous to the passage of solvent through a semi-permeable membrane into a solution. The effect in liquid helium is commonly known as the "fountain effect". Like all osmotic effects, it is numerically quite large, a temperature difference of only 0·001° K corresponding to a pressure-head of several centimetres of liquid helium.

The magnitude of the effect can be predicted by thermodynamic considerations not unlike the discussion of ordinary osmotic pressure. A closed formula can be obtained, as was shown by H. London (1939), if we suppose that transfer of superfluid between two connected vessels is not accompanied by any entropy change—that is, that it is *thermodynamically reversible*. This further assumption has been verified, both by direct measurement of the thermal changes associated with flow through a slit, Kaptiza (1941), and by a proof that a pressure-difference between two vessels connected by a "superleak" can, of itself, give rise to a temperature difference of the expected value, Daunt and Mendelsohn (1939c).

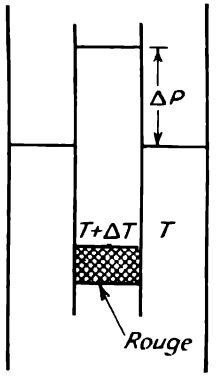

Fig. 60. The fountain effect.

The formula of H. London (1939) can be derived very simply as follows. If we *can* remove superfluid from one vessel to another, without entropy change, the work done in removing unit mass from one vessel, keeping the volume of the vessel constant, is

$$-(\partial E/\partial m)_{S,V}=-(\partial G/\partial m)_{P,T}=-g(P_1, T_1)$$

while the work of adding unit mass to the other vessel is $g(P_2, T_2)$. Thus, if two vessels are connected by a "superleak", the condition that there should be no superfluid flow, so that conditions are steady, is

$$g(P_1, T_1)=g(P_2, T_2) \tag{1}$$

For small pressure and temperature differences, this reduces to

$$\frac{\Delta P}{\Delta T}=-\frac{(\partial g/\partial T)_P}{(\partial g/\partial P)_T}=\frac{s}{v}=\rho s \tag{2}$$

which is the London formula (1939), which is obeyed for sufficiently narrow connecting slits (Meyer and Mellink (1947)). The analogy with osmotic pressure is very close, equation (1) being formally the same as that governing osmotic equilibrium, except that "change of concentration" is replaced by "temperature change". It is now natural to ask

what becomes of formula (2) if we work with a wider slit or capillary? The effect of doing this is that the flow is no longer a transfer of superfluid only, but some flow of normal fluid (as a result of the pressure difference ΔP) now becomes possible. The "osmotic analogue" is a system consisting of two solutions separated by a membrane that allows some penetration by solute as well as solvent. As is well known, under such conditions the concentrations on the two sides of the membrane are eventually equalised and the osmotic pressure disappears. A difference in pressure would, however, persist indefinitely, if we continuously supplied solute on one side of the membrane and removed it from the other side.

10.3.2. Pseudo-conduction of Heat

The analogue of such an "osmotic" experiment as this is very easily carried out with liquid helium—we have only to introduce a steady supply of heat at one end of our capillary (fig. 61). In this case, the two-fluid model predicts the following sequence of events. The "concentration" of normal fluid is higher at the hotter end, and superfluid flows through the capillary into the hotter vessel, building up the pressure. In response to this difference in pressure, the normal fluid begins to flow *out* of the hotter vessel at a rate determined by its viscosity, the pressure difference, and the dimensions of the capillary. Finally, a steady state should be reached, fixed by the following conditions:

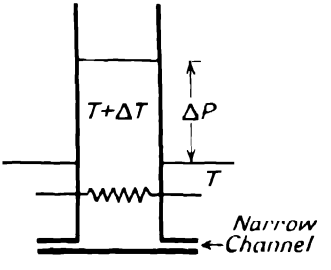

Fig. 61. Pseudo-conduction of heat in He II.

(a) The rate of transport of heat is proportional to the velocity and heat capacity of the normal fluid, since the superfluid carries no entropy. If the flow is lamellar, v_n, and therefore the rate of heat transport, should be proportional to ΔP. The latter result is found experimentally, Allen and Reekie (1939).

(b) The rates of transfer of superfluid and normal fluid are equal and opposite, so that there is *no* apparent transfer of matter at all.

(c) The pressure-difference may settle down at a value somewhat less than that given by (2). (As ΔT becomes large, the measured rate of heat transfer ceases to be proportional to ΔT, but remains proportional to ΔP.)

(d) The rates of transfer of superfluid and normal fluid are governed by the rate of conversion of superfluid into normal fluid by the heating

coil. If the entropy of the superfluid is practically zero, we have the following set of equations, if ρ_n is the density of normal fluid, ρ_s that of superfluid, so that $\rho_n+\rho_s=\rho$.

$$\text{Heat capacity of unit mass of superfluid}=0$$

$$\frac{\text{Heat capacity of unit mass of liquid helium}}{\text{Heat capacity of unit mass of normal fluid}}=\frac{\rho_n}{\rho} \qquad (3)$$

Then

$$\begin{aligned} dQ/dt &= \text{rate of heat supply} \\ &= \text{rate of transfer of normal fluid} \times \\ &\qquad \text{heat capacity per unit mass of normal fluid} \\ &= \text{rate of transfer of normal fluid} \times \rho/\rho_n \times c \end{aligned} \qquad (4)$$

where c is the heat capacity per unit mass of liquid helium. (The rate of transfer of normal fluid is related to ΔP by Poiseuille's law.)

This experiment that we are now describing is none other than a measurement of "apparent heat conductivity" already mentioned above (p. 280). In an ordinary measurement of the heat conductivity of a liquid we have a steady input of heat, but we do not take a measurement until temperatures are steady and until there is no net flow of liquid along the tube. It is usually considered sufficient evidence of this if the levels are steady (which is held to prove both the absence of any steady transfer of the liquid along the tube, and also the absence of convection effects). If, however, the two-fluid picture of liquid helium has any physical sense at all, it predicts the possibility of the transfer of heat by a "conveyor-belt" type of process, which can go on quite continuously, without being associated with periodic changes in the way that ordinary convection effects nearly always are. As we have just indicated, the process is as follows, the superfluid moves along the capillary to the hot vessel, picks up heat from the source and is changed into normal fluid, the normal fluid is driven out of the hot vessel by the excess pressure ΔP and on reaching the colder vessel is changed again into superfluid. This picture is supported by quite a variety of evidence. For example, Kapitza (1941) showed that flow of heat out of a closed vessel with an orifice (fig. 62) was associated both with an actual force on the vane near the orifice, and with a reaction force on the vessel itself. He also showed that the process of "heat conductivity" could be seriously interfered with if some other motion (besides that required

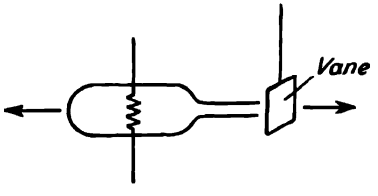

Fig. 62. Forces associated with heat flow in He II.

by this mechanism of conductivity) was also imposed on the helium, e.g. by performing the experiment in a tube having a rod lying along its axis and then repeating the experiment with the rod set into rotation.

It has also been shown, F. London and Zilsel (1948), Gorter and Mellink (1949), that this picture of heat transfer can be developed further. The considerations suggested by equations (3) and (4) can be followed up, and a "two-fluid hydrodynamics" can be developed. If we first suppose that each fluid moves independently of the other (the motion of the normal fluid being determined in the usual way by equating the force due to a pressure-gradient to the viscous forces), it is possible to account quantitatively for many of the observations on the apparent heat conductivity, the required values of the viscosity of the normal fluid being practically the same as those deduced from the oscillating-disk experiments. Since equation (2) gives a linear relation between ΔP and ΔT (which has been verified experimentally over fairly wide ranges) and since Poiseuille's law predicts a linear relation between ΔP and $\overline{v_n}$, the mean velocity of the normal fluid, the prediction of the model is that the rate of heat transfer should be proportional to ΔT. This, in fact, is the observed limiting form of the law for small v_n; in most conditions, a range of values of ΔT for which the apparent heat conductivity is constant can be clearly distinguished. For larger ΔT, we have already noted that the relation ceases to be linear. Many of the experiments could be analysed empirically in terms of the law $dQ/dt=(\Delta T)^{1/3}$, which Gorter and Mellink (1949) proposed to explain by introducing an interaction force between the two fluids proportional to the cube of their relative velocity. However, such an assumption is not in accordance with some other data (p. 296), and many of the observations on heat transfer are equally consistent with the picture that some saturation effect is setting in—for example it would be very reasonable to think that the superfluid could not move at more than a certain velocity without losing its superfluid properties altogether, or, again, completely reversible flow might be possible for only a certain *range* of velocities, dissipative effects setting in for higher ones, Hung, Hunt and Winkel (1952). We postpone discussion of these difficult points, which must be regarded as still unsettled, and on which very little theoretical guidance is available (pp. 299–300). Another difficulty that should be mentioned here is that the ordinary concept of "viscosity of the normal fluid" apparently ceases to be properly applicable for slits of less than a certain width ($\sim 10^{-4}$ cm). For narrower slits, the heat-transfer measurements can still be analysed in terms of an effective viscosity, η_n, of the normal fluid, but this is now much smaller than that deduced from the oscillating-disc experiments, and seems to depend on the width of the slit.

10.3.3. "Second Sound"

It will thus be seen that the two-fluid picture is capable of correlating a great many experiments, but that there are very definite limitations on its applicability. In this respect, it may be compared with the Londons' electromagnetic equations for a superconductor (p. 252). Before describing some of the ways in which the two-fluid picture might be improved, we shall consider a further set of experiments that can be analysed in terms of the two-fluid picture as it stands. The existence of a further effect was, in fact, predicted by Tisza (1938) as a consequence of the two-fluid picture. The predicted effect is known, not very happily, as "second sound". It consists of the propagation of temperature differences in liquid He II *with a definite wave-velocity and without appreciable attentuation*. To a first approximation, this propagation is governed by the wave-equation rather than by the heat conduction equation. (It is *not* possible to get such an effect with the heat conduction equation, even if we take a very large numerical value for the heat conductivity. It is readily verified that any solutions of the heat-conduction equation for which the temperature is a periodic function of the time cannot be a purely periodic function of the distance, but must contain instead factors like $e^{-kx} \sin kx$ which are always strongly attenuated in distances of the order of a wavelength.)

The effect predicted by Tisza (1938) and independently by Landau (1941) was verified experimentally by Peshkov (1946), and has since been studied by many other workers. The source of second sound has almost always been an alternating current passed through a resistance. This does not yield a sinusoidal temperature oscillation, but, since the dispersion is very small, this does not interfere with accurate measurements of the velocity of propagation. Various pulsing and stationary wave techniques, the analogues of those in use for ultrasonic studies, have gradually been introduced, and the measurements have been extended from the transition temperature down to about 0·2°K. For reviews of recent work, see, for example, Report of M.I.T. Low Temperature Conference (1949), Report of Oxford Conference on Low Temperatures (1950), Report of Brussels Conference on Ultrasonic Vibrations (1951), Report of Schenectady Conference on Low Temperatures (1952), Report of Third International Conference on Low Temperatures at Rice Institute, Texas (1953). The various observations on the velocity of propagation show close agreement down to about 0·4°K (fig. 63), but, below this temperature, it appears that dissipative effects are becoming important and that the situation can no longer be described by means of a simple wave equation, Gorter (1952), Atkins (1953 a). It may well be that mean free path effects are intervening, or the true heat-conductivity is becoming large. See p. 309.

As we shall see below, we can deduce from the two-fluid picture the following equation for the velocity of propagation of second sound

$$c_2^2 = \frac{\rho_s}{\rho_n} \frac{s^2}{(\partial s/\partial T)_P} \tag{5}$$

where s is the entropy of liquid He II per unit mass. Now $(\partial s/\partial T)_P$ is C_p/T and is a directly observable quantity and, by a numerical integration, assuming as usual that $s \to 0$ as $T \to 0$, s itself can be determined from the specific-heat data, and c_2 also be obtained from purely thermal measurements. Thus, equation (5) enables us to deduce the quantity ρ_s/ρ_n from *purely thermal* measurements, while the oscillating-disc experiments enabled us to deduce the same ratio from *purely mechanical*

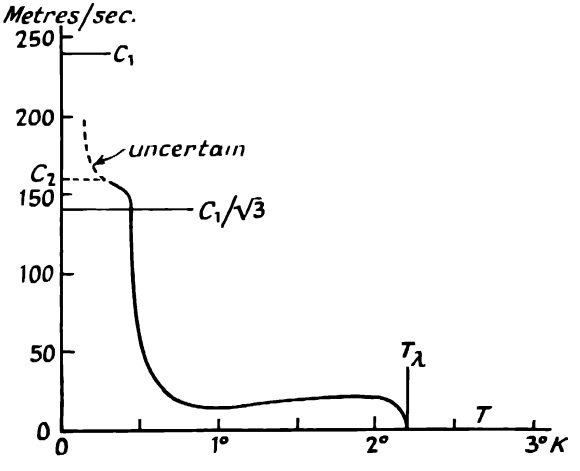

Fig. 63. Variation of c_2 with temperature.

measurements. A comparison has been made, see, for example, Gorter, Mellink and Kasteleijn (1950), and the two available methods of measuring this quantity agree very satisfactorily. It thus seems certain that this ratio does indeed measure some *actual physical property of* liquid He II, and this remark remains true whether we accept the two-fluid picture, or whether we ultimately interpret the ratio ρ_s/ρ_n in terms of some other physical concept. It is hard to think of two methods of measuring the same physical quantity that are more unlike one another than are these two, one purely mechanical, the other purely thermal. We shall see below (p. 296) that measurements with the "thermal Rayleigh disc" confirm these values of ρ_s/ρ_n and thus afford further evidence that this ratio represents some real physical property of the liquid.

10.3.4. Two-fluid Hydrodynamics

We shall now develop the numerical consequences of the two-fluid hypothesis as preliminary steps towards constructing a physical theory. It is not yet possible to be quite certain about the non-linear effects, corresponding, for example, to the Bernouilli terms in ordinary hydrodynamics, and it appears, in fact, that the information at present available is insufficient to enable their form to be determined uniquely. The "linearised" equations, corresponding to the "acoustic approximation" (or assumption of very small amplitudes) of ordinary hydrodynamics can, however, be obtained uniquely, and we shall first undertake this task. Considerations of conservation of matter, lead, by a generalisation of the ordinary arguments of hydrodynamics, to the result:

$$\frac{\partial \rho}{\partial t}+\operatorname{div}(\rho_n \mathbf{v}_n+\rho_s \mathbf{v}_s)=0 \qquad (6a)$$

Various derivations of the remaining equations of motion have been given. We shall follow that of Nakajima, Tomita and Usui (1950). This is to take a volume element that is *fixed in space*, to take account of the flows of the two fluids into and out of this volume element and to apply the laws of thermodynamics and the conservation of momentum. We also make use of Kapitza's observation (1941) that the entropy of the superfluid component is negligible. This means either that the entropy associated with our volume element must have been produced there by irreversible processes, or else must have been transported thither by the motion of the normal fluid. For simplicity, we confine ourselves to the case of purely *reversible* processes, the necessary modifications if we wish to take account of true heat conductivity, viscosity, or mutual friction between the two fluids being clearly given in the paper by Nakajima *et al.* (1950). (The reader studying this paper should note that equation (2.1) is no longer considered to be of universal validity. The alleged thermodynamical proof of it is faulty, see Dingle (1952), but it is a satisfactory approximation between 1°K and the transition temperature. Equation (2.2) of that paper also cannot be used below about 0·6° K.)

Equation (6) may be split up into

$$\frac{\partial \rho_n}{\partial t}+\operatorname{div}(\rho_n \mathbf{v}_n)=\Gamma; \qquad \frac{\partial \rho_s}{\partial t}+\operatorname{div}(\rho_s \mathbf{v}_s)=-\Gamma \qquad (6b)$$

where Γ is the rate of conversion of superfluid into normal fluid per unit volume. This may occur as a result of heat being developed by irreversible processes, *or* as a consequence of the breakdown of the relationship (Nakajima *et al. et al.*: eqn. (2.1)),

$$\rho_n/\rho \approx s/s_\lambda \qquad (7)$$

which only holds above 1°K. (s_λ is the entropy per unit mass at the transition temperature). Applying the principle of conservation of momentum to our small volume element fixed in space (the rate of change of momentum within that volume is to be equated to the net force acting on it), we find

$$\rho_n\left(\frac{\partial}{\partial t}+\mathbf{v}_n.\text{grad}\right)\mathbf{v}_n+\rho_s\left(\frac{\partial}{\partial t}+\mathbf{v}_s.\text{grad}\right)\mathbf{v}_s+\Gamma(\mathbf{v}_n-\mathbf{v}_s)=-\text{grad}\,P \quad (8)$$

where the first two terms on the left-hand side take account of the net rates at which momentum is changing, as a result of changes in $\mathbf{v}_n$ and $\mathbf{v}_s$ with time, and of the net rates at which it is carried into the volume element, while the third term takes care of the effect of conversion of superfluid into normal fluid within the volume, momentum, as well as energy, having to be supplied or taken away to effect such a conversion, if $\mathbf{v}_n$ differs from $\mathbf{v}_s$.

If we assume further that no irreversible processes are taking place, and that the entropy is entirely carried by the normal fluid, we must write

$$\frac{\partial(\rho s)}{\partial t}+\text{div}(\rho s\mathbf{v}_n)=0 \quad (9)$$

If (7) were valid, (9) would imply that $\Gamma=0$. So far, there appears to be no doubt about the correctness of our equations. A fourth equation can be obtained by applying the principle of conservation of energy, and various workers have claimed that, if both fluids are in motion, the internal energy per unit volume must be corrected by the term

$$\rho_n\left(\frac{\mathbf{v}_n-\mathbf{v}_s}{2}\right)^2$$

See, for example, Landau (1941), Zilsel (1950; 1953), F. London (1955). If we include such a term, the equation of motion of the superfluid component is found to be

$$\rho_s\left(\frac{\partial}{\partial t}+\mathbf{v}_s.\text{grad}\right)\mathbf{v}_s+\frac{\rho_s}{\rho}\,\text{grad}\,P-\rho_s s\,\text{grad}\,T=0$$

whereas, if we omit it, Temperley (1951), Nakajima *et al.* (1950) we get instead

$$\rho_s\left(\frac{\partial}{\partial t}+\mathbf{v}_s.\text{grad}\right)\mathbf{v}_s+\frac{\rho_s}{\rho}\,\text{grad}\,P-\rho_s s\,\text{grad}\,T+\frac{\Gamma}{2}(\mathbf{v}_n-\mathbf{v}_s)=0 \quad (10b)$$

In either case, the equation of motion of the normal fluid can be obtained by subtraction of this equation from (8). There appears to be very little evidence for deciding between (10a) and (10b). The former equation follows if, in addition to the conservation laws, we assume

$$\text{curl}\,\mathbf{v}_s=0 \quad (11)$$

the equation appropriate for irrotational motion of a perfect fluid. Equation (10b) is the correct consequence of the conservation laws if we assume that the internal energy and entropy of the *moving* fluids are the same functions of P and T as they are when the whole liquid is at rest, whereas equation (10a) is the correct consequence of assuming equation (11) in addition to the conservation laws. As far as the writer knows, there is little direct experimental evidence either for or against equation (11), although it has apparently been taken for granted by some writers that it *must* be correct. The grounds for such a belief are not clear to the author, and appear to contain an element of mysticism. We do know, from classical hydrodynamics, that a perfect fluid cannot *acquire* nor *lose* any vorticity as the result of any *motion of the boundaries*, but there is no means of knowing *a priori* what happens if the *temperature* of a small volume of liquid helium in *rotational motion* is suddenly changed. ρ_n/ρ_s will be altered, and it is, at present, an almost open question whether, if *normal fluid* is converted into *superfluid*: (a) the vorticity "stays with" this superfluid, equation (11) being untrue; (b) the superfluid obeys equation (11) always, in which case some vorticity must be transferred to the remaining normal fluid, in order to satisfy the principle of conservation of angular momentum. Many experiments have been proposed, and a few actually tried, to search for effect (b). So far the results appear to be negative, Andronikashvili (1952). The only other evidence that might perhaps have a bearing on the form of these non-linear terms seems to be the behaviour of second-sound pulses of large amplitude. D. V. Osborne (1951) found evidence of effects analogous to the "shock-fronts" occurring in ordinary media, and the phenomenon was treated theoretically by Temperley (1951) and Khalatnikov (1951). An experimental test of the theory is, in principle, possible but only a few data exist. It may also be necessary to include in our equations the terms (corresponding to those involving Γ in (10b) and (8)) which result from the interconversion of superfluid and normal fluid in the shock-front itself. This point seems worthy of further study.

We leave aside these very difficult points associated with the non-linear terms in equations (6) to (10a), and consider the consequences of these equations if they are "linearised" in the manner customary in the ordinary "textbook" theory of sound. (The interpretation of the very interesting experiments of Pellam and Morse (1950) on the "thermal Rayleigh disc", which we shall discuss below (p. 296), is *not* affected by our choice of equation (10a) or (10b), because these depend on the *Bernouilli terms* occurring in equation (8), about the existence of which there is no dispute.) If a definite physical *model* is assumed it may be possible to compute the non-linear terms exactly. See Dingle (1952) for an example of this, see also Zilsel (1953).

10.3.5. The Linearised Equations and their Consequences

Exactly as in the theory of ordinary sound, we neglect all powers and products of the stream-velocities $\mathbf{v}_s$ and $\mathbf{v}_n$, and all products of these quantities with quantities like grad P and grad T, which are themselves small if the departures from equilibrium are small. From equation (6):

$$\frac{\partial \rho}{\partial t}+\rho_n \operatorname{div} \mathbf{v}_n+\rho_s \operatorname{div} \mathbf{v}_s=0$$

From equation (8):

$$\rho_n \frac{\partial \mathbf{v}_n}{\partial t}+\rho_s \frac{\partial \mathbf{v}_s}{\partial t}=-\operatorname{grad} P \tag{12}$$

so that

$$\frac{\partial^2 \rho}{\partial t^2}=\nabla^2 P \tag{13}$$

From equation (9):

$$s\frac{\partial \rho}{\partial t}+\rho \frac{\partial s}{\partial t}+\rho s \operatorname{div} \mathbf{v}_s=0$$

using (6) for $\frac{\partial \rho}{\partial t}$;

$$\frac{\partial s}{\partial t}=\rho_s s \operatorname{div}(\mathbf{v}_s-\mathbf{v}_n) \tag{14}$$

From equation (10a) or (10b):

$$\frac{\partial \mathbf{v}_s}{\partial t}=-\frac{1}{\rho}\operatorname{grad} P+s \operatorname{grad} T=-\operatorname{grad} g \tag{15}$$

using equation (12) to eliminate grad P, and then equation (14) to eliminate $(\mathbf{v}_s-\mathbf{v}_n)$,

$$\frac{\partial^2 s}{\partial t^2}=\frac{\rho_s}{\rho_n} s^2 \nabla^2 T \tag{16}$$

These equations have been often derived, but a number of points about them call for comment. Equation (15) shows that the acceleration of the superfluid is proportional to the gradient of g, or to the "osmotic driving force". Indeed, the equation seems to have originally been derived by an argument similar to that used in deriving the first London equation for a superconductor, and running somewhat as follows: An osmotic force ordinarily leads to a *rate of flow* proportional to the osmotic force (leading to an equation of motion of "diffusion" type). A motion of the superfluid can occur without dissipative effects, so that a difference of osmotic pressure should *accelerate* it. (See, for example, Landau (1941).) This argument can be criticised in a number of ways and, even if we accept it as valid, it is extremely difficult to see physically why the factor of proportionality between $\partial \mathbf{v}_s/\partial t$ and grad g should be just unity

and should not involve ρ_s explicitly. It seems better, as we have done, to derive the equation (15) as a consequence of the laws of conservation of energy and entropy, in conjunction with equation (9) (stating that the superfluid carries no entropy). The latter equation becomes physically reasonable when we consider possible models of liquid helium theoretically, meanwhile we shall regard it simply as a deduction from experiment.

Equations (13) and (16) can now be reduced to the form of wave equations by means of the equation of state, for we may write, after rejecting terms involving $(\partial P/\partial t)^2$ and $(\partial T/\partial t)^2$:

$$\frac{\partial^2 T}{\partial t^2}\left(\frac{\partial \rho}{\partial T}\right)_P+\frac{\partial^2 P}{\partial t^2}\left(\frac{\partial \rho}{\partial P}\right)_T=\nabla^2 P \quad \text{from (13)} \tag{17}$$

$$\frac{\partial^2 T}{\partial t^2}\left(\frac{\partial s}{\partial T}\right)_P+\frac{\partial^2 P}{\partial t^2}\left(\frac{\partial s}{\partial P}\right)_T=\frac{\rho_s s^2}{\rho_n}\nabla^2 T \quad \text{from (16)} \tag{18}$$

a typical solution of which is readily found by substituting

$$P=P_0+(\Delta P)\exp(i\omega t-i\omega x/c)$$

$$T=T_0+(\Delta T)\exp(i\omega t-i\omega x/c)$$

into (17) and (18), giving us a quadratic equation for c. If, as is usually the case, the coefficient of expansion of liquid He II is numerically very small, $(\partial\rho/\partial T)_P$ and $(\partial s/\partial P)_T$ can both be neglected, and equations (13) and (16) become quite independent of one another. Under these conditions equation (13) becomes identical with the ordinary acoustic equation, and the velocity of propagation of sound is given by $c_1^2=(\partial P/\partial\rho)_T$. If the coefficient of expansion is zero, this is identical with the usual expression $(\partial P/\partial\rho)_s$. Inspection of equation (6) shows that the stream velocity associated with such a sound wave is $(\rho_n \mathbf{v}_n+\rho_s \mathbf{v}_s)/\rho$, that is, the *mean rate of transport of matter*, which is what we might expect. Equation (16) or (18) will lead to a velocity of propagation

$$c_2^2=\frac{\rho_s}{\rho_n}\frac{s^2}{(\partial s/\partial T)_P} \tag{19}$$

a result, which, as we have seen, is confirmed by experiment. Equation (14) then shows us that the stream velocity associated with a change in temperature ΔT is $(\mathbf{v}_s-\mathbf{v}_n)$, which is reasonable because a relative flow of the two fluids leads to local differences in ρ_s/ρ_n, which are equivalent to local differences of temperature.

The fact that equations (13) and (16) are very nearly independent of one another led to the introduction of the terms "first" and "second" sound for these two possible modes of motion. Although the nomen-

clature is in some respects unfortunate ("second sound" being a purely thermal effect), it does serve to keep before us the fact that these two modes of motion are liable to be *coupled* if any of our idealisations break down. Among possible results of such coupling we must particularly notice the fact that the expected velocities of propagation of our two modes of motion will no longer be given exactly by c_1 and c_2, nor will these modes refer to purely acoustical or purely thermal modes of motion. Among mechanisms that could give rise to such coupling in appropriate circumstances we may mention:

(a) The effect of viscosity of the normal fluid. To allow for this, terms depending only on $\mathbf{v}_n$ have to be added to grad P in (8), and these would lead to a coupling between our two modes of motion.

(b) The effect of *true* thermal conductivity. It has long been recognised that this can, in all substances, act as a mechanism for dissipating ordinary sound, and it is also obvious that it will introduce a dissipative term proportional to $\partial T/\partial t$ (besides the term proportional to $\partial^2 T/\partial t^2$ already present) into the equation for second sound. It is to be expected that it will lead to coupling, for the same physical reason that a resistance common to two otherwise independent electrical circuits leads to coupling between them. The equations are given explicitly by Nakajima *et al.* (1950).

(c) It is possible that the densities ρ_s and ρ_n do not at once attain their equilibrium values if P or T (or both) suddenly change. In such a case, it might not always be permissible to neglect terms such as those involving Γ in (8) or (10b), even though they are essentially non-linear. A mechanism of this kind (equivalent to the assumption that ρ_n/ρ_s does not at once follow alterations in P) was assumed by Khalatnikov (1950) in order to explain the "extra" dissipation of ordinary sound that could not be accounted for by the viscosity of the normal fluid.

The fact that c_2 is in satisfactory accord with theoretical expectations down to temperatures of about 0·5°K, but below that shows a decided tendency to approach the limiting value c_1, rather than the value $c_1/\sqrt{3}$ that is to be expected theoretically (see p. 306), may be a result of one of these dissipative mechanisms becoming more and more important as $T \to 0$. Another possibility is that, as $T \to 0$, these dissipative processes fail to be described by concepts like viscosity and thermal conductivity for the same sort of reason that these concepts fail in a gas at very low pressures (mean free path effects). We met a similar situation when discussing the high-frequency behaviour of metals at low temperatures (p. 258). It is not possible to foresee whether such situations are likely in liquid helium without a detailed model. We shall return to this point later on (p. 309).

10.3.6. Further Experiments confirming the Validity of the Two-fluid Concept

We have already noted that the linearised equations, when supplemented by terms describing the viscous drag on the normal fluid, are capable of describing the apparent heat conductivity for slits and tubes of a certain range of width and radius. If the channel becomes too wide it is necessary to postulate, in addition, a critical velocity of superfluid flow, a mutual friction between the fluids or some other non-linear effect. No hypothesis that has yet been tried seems to be capable of interpreting all the experiments. For example, if we consider the oscillating pile of discs, the effects that occur when the amplitude of the oscillation is increased, Hollis-Hallett (1952), cannot be described at all well by the mutual friction hypothesis of Gorter and Mellink (1949). We have already noticed the difficulty of interpreting the apparent heat conductivity for very fine slits (p. 287). It will be seen, therefore, that the two-fluid model certainly has some physical significance because it is capable of correlating a number of experiments of very different sorts. We must also admit that, like the London theory of superconductivity, the model is phenomenological only and, furthermore, that there are certain experiments that it fails to describe properly. Recently, the viscosity of the normal fluid has been measured by a third method, a rotating-cylinder type of viscometer, Hallett (1953 a, b). These experiments are in good agreement with the general two-fluid picture, and, although some points are not yet explained, the validity of the concepts of the viscosity of the normal fluid, and of the ratio ρ_s/ρ_n as representing definite physical properties of the liquid, have received further confirmation, but the way in which this picture breaks down as velocities increase remains obscure. The numerical value of the stream-velocity at which the simple two-fluid picture begins to break down seems to depend on the type of experiment. For the viscosity measurements it is evidently of the order of a fraction of a cm/sec, but in second sound measurements it can be of the order of metres/sec.

A further experiment, of a different nature from anything that we have so far described, which was made by Pellam and Morse (1950), also provides strong confirmation of the validity of the two-fluid model. This consists of a direct measurement of a "second-sound field" by means of a Rayleigh disc. As is well known, a perfect fluid flowing past a disc does not exert any *force* on it, but it does exert a *couple* tending to twist the disc broadside on to the flow. (Lamb, *Hydrodynamics*, 6th Ed. (1945).) For an ordinary fluid this couple is proportional to the Bernouilli term ρv^2, and is independent of the sign of v, and is therefore finite for an oscillating velocity-field such as exists in a sound-wave. On the two-fluid picture, the torque to be expected should be proportional

to $\rho_s v_s^2 + \rho_n v_n^2$ and this prediction has been accurately confirmed experimentally. As far as the author knows, this is the nearest we have come to a direct proof of the physical existence of the quantity v_s, and the experiment also confirms the physical reality of the quantity ρ_s/ρ_n. Experiments such as those described by Kapitza (1941) could, in principle, be conducted and analysed in a way that would enable us to measure v_n quantitatively by observing the force it exerts on a solid body. See Hall (1954). Equally, a measurement of pseudo-heat conductivity may be regarded as a fairly direct measurement of v_n, since the heat-content of unit mass of liquid He II is known experimentally. v_s, however, corresponds to *no* heat flow, and to *no* force on a solid obstacle.

10.4. Film Phenomena

In using the two-fluid hypothesis, we suppose that the normal fluid is at rest at solid boundaries, but that the superfluid is capable of slipping along them, and it is natural to ask ourselves whether this state of affairs persists right up to the solid, or whether the liquid in the immediate neighbourhood of a solid boundary is changed in any fundamental way. It is now known that, below the transition temperature, any solid surface that is in contact with liquid helium, or which is in a region below the transition temperature to which He vapour has access, is covered by a film of helium of the order of 100 atoms thick. This film is *mobile* and, under suitable experimental conditions, will run over a surface at a mean velocity of the order of 20 cm/sec. For example, if a solid surface enters a region where the temperature is above the transition temperature the film evaporates off, and is constantly replaced by fresh film moving in from the colder portions. (As a matter of fact it is this mechanism that sets practical limits on the reduction of temperature that can be attained by pumping on liquid helium.) Again, many experiments have been done on the lines of that illustrated in fig. 64. See for example Mendelsohn and Daunt (1939 a, b). With such experiments it has been found that the film will cover the entire inside and outside surfaces of the vessel and that, everywhere below the level of the bulk liquid, it is capable of forming into drops, so that we apparently have the liquid running up the sides of the vessel and dripping off outside (hence the newspaper headline: "The liquid that flows uphill"). It has also been established that, at any given temperature, the rate of film transfer is proportional to the smallest *perimeter* over which it has

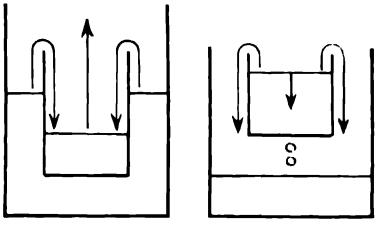

Fig. 64. Experiments on film flow.

to pass. For example, in a vessel shaped as shown in fig. 65, the rate of transfer would be proportional to the *inner circumference at the level* AB. This indicates that at each temperature, there is an upper limit to the "transfer constant" (i.e. mean velocity of transfer × film thickness). The rate of transfer does, however, also vary slightly with the height the film has to "climb" above the bulk liquid before finding a downhill portion of path. An ingenious experiment by Daunt and Mendelsohn (1946) proves that film flow *can* be maintained even if the net hydrostatic pressure difference between two vessels connected by a film is no more than a fraction of a millimetre head of liquid helium. Thus, one is tempted to make comparisons with superconductors (critical velocity, flow without pressure-head). Some recent experiments by Picus (1953), however, do indicate that a finite pressure-head, of the order of 0·1 mm of liquid helium, *may* be needed to initiate flow.

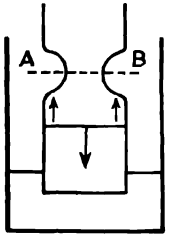

Fig. 65. Film flow limited by constriction.

The relationship between film flow and bulk liquid flow has not been fully worked out, for the practical reason that the film thickness is usually of the order of 10^{-6} cm and it is difficult to make a channel of *known* width less than about 10^{-4} cm, so that the probable transition region is extremely difficult to approach experimentally. (Some recent experiments with channels made of packed rouge particles, Chandresekhar and Mendelsohn (1953), proved unexpectedly hard to interpret.) The experiments of Allen and Misener (1939), followed up by Atkins (1950), show that, with a proper geometry, *oscillations* of level can occur in two vessels connected by film, as we might expect if a "superflow" process is involved, and that such experiments can be interpreted fairly satisfactorily by two-fluid hydrodynamics, treating "film flow" on the same footing as "bulk flow", and assuming the same value of ρ_s/ρ_n for both. A very recent experiment (Lane and Dyba (1953)) shows that, fig. 66, film flow is capable of "feeding" a capillary whose bottom end does not reach down into the bulk liquid.

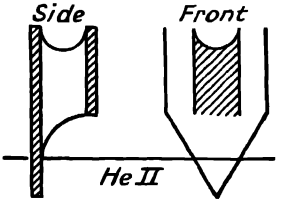

Fig. 66. Lane and Dyba's experiment.

Mention must also be made of the beautiful experiments of Jackson, Burge, Henshaw and Ham (1951; 1953) in which, by an optical method, similar to that used in the study of thin films of certain proteins, the film thickness can be measured optically, its variation with height above the bulk liquid determined, and various ancillary phenomena, such as

the incipient formation of drops, are actually made visible. The variation of film thickness with height above bath level is definitely established, and seems to follow a law of the type $t \propto h^{-1/3}$, a law which is in reasonable accord with theory, Schiff (1941), Temperley (1949),* Band (1951), this relation agreeing reasonably well with indirect deductions about film thickness and its variation with height made by Atkins (1950) from his oscillation experiments.

Various attempts have been made to determine in what way the film phenomenon is related to ordinary adsorption of vapour; see a review article by Long and Meyer (1952); also Bowers (1953). Unfortunately, there is a small region in the P-T diagram when one is very near to saturation, where the equilibrium film thickness is changing very rapidly with pressure, but where it seems to approach its equilibrium thickness extremely slowly with time and is very sensitive, for example, to incident radiation, Bowers (1953). This is to be expected if the adsorption energy of the top layers is very small, so that the "thermodynamic driving force" is small also (p. 50), and the results of such experiments are complex and hard to interpret. It is interesting to mention that abnormal properties of an adsorbed helium film were predicted by Lennard-Jones and Devonshire (1937), at about the time that film effects were being discovered. They pointed out that, on an ordinary solid surface, the adsorption energy would be very small and an individual helium atom would not be bound to an individual site, like an ordinary adsorbed atom, but would be free to run about over the surface in the same sort of way that a conduction electron can run through the crystal lattice in a metal, as a result of the "tunnel-effect". In ordinary adsorption, the atom is strongly bound to a particular site, and would have to surmount a high potential barrier in order to reach another site.

10.5. Critical Velocities

So far, no theory has given more than rough preliminary explanations of any of the critical velocity effects that are observed or inferred from the experiments. With a given geometry of apparatus there may be more than one critical velocity involved; see, for example, Bowers and Mendelsohn (1950; 1953). These experiments seem definitely to require the existence of *two* critical velocities, a lower one at which irreversible effects begin to set in, and a higher one which marks the limiting rate of flow possible. We have already noted a similar situation with the analysis of the "heat conduction" processes (p. 287). What is even more puzzling is the wide range of values of "critical superfluid velocity" (or critical value of $\mathbf{v}_s$) that can be obtained from different

* The following misprints occur in this paper. Eqn. (4): For 10^{-7} read 10^{7}. For 10^{6} read 10^{-6}.

types of experiment. Thus, from the oscillating-disc and rotating-cylinder experiments Hallett (1950; 1952; 1953 a, b) one would think that the simple two-fluid hydrodynamics is already beginning to fail at velocities of the order of 0·2 cm/sec. Film flow and experiments on flow through tubes suggest critical velocities of the order of 10 cm/sec, while the "second-sound" experiments seem to indicate that the two-fluid hydrodynamics is working tolerably until we reach amplitudes equivalent to stream velocities of the order of 100 cm/sec. At various times, a relation $v_c d$=constant has been proposed, where d is some dimension like a channel width. While experiments on flow through tubes (see Atkins (1950; 1951), who also reviews earlier data) do give some support to a relation of this kind as a means of correlating some of the phenomena, there are clearly other "critical velocities" that are *not* so described.

10.6. Attempts at Fundamental Theories

Attempts at interpreting the strange mixture of reversible and irreversible effects that we have outlined above have followed three main lines, analogous to the attacks on the ordinary liquid problem.

(a) Attempts have been made to develop a "gas-like" model of the liquid, based on the fact that an assembly consisting of *non-interacting* particles obeying Bose-Einstein statistics already shows some of the features of actual liquid helium, including a transition of co-operative type. Tisza (1938; 1947), F. London (1938), Fraser (1951 a, b), Prigogine and Philipott (1952; 1953 a, b).

(b) Attempts have been made to modify the Debye model of a liquid (p. 75), in which sound-waves are used to represent the effect of interactions between the atoms: Landau (1941; 1947), Landau and Khalatnikov (1949 a, b), Kronig and Thellung (1950), Ziman (1953).

(c) Attempts have been made to show that the properties of liquid He II are in some way related to those of the two-atom distribution function, Born and Green (1947; 1948), Penrose (1951), Feynman (1953 a, b, c; 1954).

All of these approaches have made encouraging progress, and it seems that a synthesis of the three points of view should not be too difficult. Temperley (1952 a, b; 1953) has examined the relationships between approaches (a) and (b) and has indicated a possible way of compromising between them. Both of the initial approximations (a) and (b) are poor. Attempts to improve the perfect gas model, by replacing the free-atom wave functions by functions similar to those occurring in a metal, lead to the conclusion that both "nearly free particle" and "tight binding" approximations are poor, and the intermediate case can only be handled numerically. Attempts to apply standard methods of

perturbation theory also lead to no very definite results because such methods "blow up" when the interaction between two particles is sufficient to lead to a bound level. The approach based on the Debye model has also been developed considerably, but, here again, the initial approximation is not good. The Debye model of a solid really involves the concealed assumption that the potential energy of, for example, a crystal lattice can be sufficiently accurately expressed as a *quadratic* function of the displacements of all the atoms from their equilibrium positions. This is a reasonable approximation for a solid, for which the interatomic forces are strong, so that only *small* displacements of a given atom from its equilibrium position are likely. For a liquid, the interactions are weaker, and the assumption of small displacements begins to fail, and for liquid helium, the interactions are very weak and the interatomic spacing is large. A possible new approach was indicated by A. Bijl (1940) and further developed by P. J. Price and Onsager (both unpublished) and by Feynman (1954). Bijl (1940) showed that perturbation theory could be arranged in such a way that the data to be "fed in" to the theory consists not of an assumed interaction between two atoms, as in other forms of perturbation theory, but observations on the X-ray or neutron scattering by the liquid.

10.6.1. Simon's Explanation of the Failure of Liquid Helium to Solidify

The correct explanation of the persistence of the liquid phase down to absolute zero seems to have been first given by Simon (1934), but it has been put in a number of different forms by various other workers. If we suppose, for the moment, that we had just two helium atoms, the wave function describing them would behave, as a function of their distance apart, in very much the same way as the well-known wave function of the deuteron. In fig. 67 the interaction energy and wave function are plotted as functions of the distance between the two nucleons. As is well known, the interaction energy is only just sufficient to give rise to a bound state, and the binding energy is small in comparison with the interaction energy, the terms $(\hbar^2/2m)\nabla^2\psi$ and $-V\psi$ in the wave equation nearly cancelling. This has two consequences:

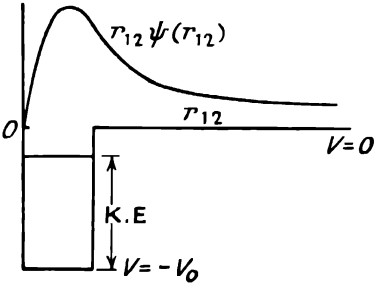

Fig. 67. Wave function of deuteron.

(a) The wave function remains appreciable even though the mutual distance of the nucleons is long compared with the range of their interaction.

(b) The predictions of theory are not greatly altered by changes in the assumed *form* of the potential well representing the interaction.

The various theories of liquid helium may perhaps all be regarded as attempts to describe the analogous situation when we have many atoms interacting with one another with an interaction of about the critical strength. The large kinetic energy term is usually referred to as zero-point energy. Such a term exists in any quantum mechanical assembly (for example the term $(9/8)k\Theta$ in the ordinary Debye solid) but is particularly important in liquid helium because of the lightness of the atoms and the relative weakness of the attractive forces. The value of this zero-point energy and the mean energy due to the interactions have both been estimated in various ways, Simon (1934), F. London (1936), all giving the following approximate results:

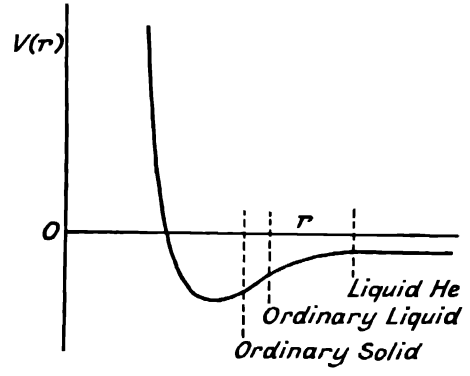

Fig. 68. Relationships between interaction function and mean intermolecular distance.

Interaction energy at observed density of liquid: −80–90 cal/mole
Zero-point energy at observed density: +60–70 cal/mole
Net internal energy at observed density: 15–20 cal/mole

The lattice constant for a simple cubic lattice of the observed density of the liquid is 3·6 ångström units, at which distance the repulsive forces between the atoms are quite negligible. The equilibrium lattice distance is therefore fixed by a balance between the attractive forces and the zero-point energy. (If the mean density were increased, the zero-point energy would rise also.) For all ordinary liquids and solids the mean lattice distance is fixed by a balance between attractive and repulsive forces. Since the repulsive forces always vary with high inverse powers of the distance this means, in practice, that in equilibrium, the "hard cores" of neighbouring atoms are nearly in contact. Fig. 68 compares the interactions of two neighbouring atoms in an ordinary

solid or liquid with the interactions between two neighbouring helium atoms, at the observed liquid density.

The decision whether or not an ordinary liquid should solidify depends on some balance between energy and entropy, i.e. on whether the loss of entropy on forming a more ordered structure is balanced by a corresponding gain in energy. Although no quantitative theory is yet available, it is clear that the relationship between the attractive and repulsive forces determines both the density at which the formation of a crystal lattice is thermodynamically profitable, and also what type of lattice it is most profitable to form. In liquid helium, the repulsive forces are very small, and these considerations cannot operate. It is therefore intelligible that an ordered crystal lattice does not form until the atoms are pushed together by external pressure until the true repulsive forces become appreciable. Qualitatively, if we think of a helium atom moving around amongst several neighbours, a slight change in its position makes no very big difference in the zero-point energy. In an ordinary liquid, a typical atom cannot move far without encountering the repulsive fields of its neighbours, and a small shift in position may imply a big energy-change. Thus repulsive forces *may* have a much stronger ordering influence than has the zero-point energy effect. This seems to be as near as we can hope to get to an explanation of the *absence* of solidification in liquid helium, until such time that we get a better insight into the process of solidification in ordinary liquids than is afforded by the very rough theories at present available (Chapter V).

10.6.2. The Bose-Einstein Condensation

Conventional statistical mechanics predicts a curious phenomenon even in a perfect gas if its atoms are described by symmetrical wave functions, i.e. obey Bose statistics, and it was suggested by F. London (1938) that this might have some connection with the properties of liquid helium II. The energy-levels for particles in a cubical box of side d are given by

$$E_{p,q,r}=(h^2/8md^2)(p^2+q^2+r^2) \qquad (20)$$

where p, q, r, are positive integers (not zero). The partition function associated with such a set of energy-levels is given by

$$\log f=-\sum_{p,q,r}{}' \log\left[1-\lambda\exp\left\{-\frac{h^2(p^2+q^2+r^2)}{8md^2kT}\right\}\right] \qquad (21)$$

This can usually be evaluated with sufficient accuracy by expanding the logarithm in ascending powers of λ, and replacing the summations over p, q, r by integrals. We must, however, remember that the Euler-Maclaurin sum formula shows that this process must be carried out

with care, because correcting terms may have to be applied at both ends of any continuous range of integration that replaces a summation over discrete values. Investigation shows that the only correcting term that need be considered is that for which $p=q=r=1$, and that expression (21) can be approximated sufficiently accurately for all purposes by

$$\log f=-\log\left[1-\lambda\exp\left\{-\frac{3h^2}{8md^2kT}\right\}\right]+\sum_{s=1}^{\infty}\int_0^{\infty}\int_0^{\infty}\int_0^{\infty}\frac{\lambda^s}{s}\exp\left\{-\frac{sh^2(p^2+q^2+r^2)}{8md^2kT}\right\}\mathrm{d}p\mathrm{d}q\mathrm{d}r$$

For a large assembly $d\to\infty$, and the exponential factor in the first term can be dropped, while the result of performing the integrations leads to

$$\log f\approx-\log(1-\lambda)+V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\sum_{s=1}^{\infty}\lambda^s s^{-5/2} \qquad (22)$$

Where $V=d^3$, the volume of the vessel. λ is to be determined from the usual equation $N=\lambda(\partial/\partial\lambda)(\log f)$ leading to

$$N=\frac{\lambda}{1-\lambda}+\left(\frac{2\pi mkT}{h^2}\right)^{3/2}V\sum_{s=1}^{\infty}\lambda^s s^{-3/2} \qquad (23)$$

This equation can always be solved for λ, but, for N and V very large, an analytic singularity occurs in f at a temperature T_c given by

$$\frac{N}{V}=\left(\frac{2\pi mkT_c}{h^2}\right)^{3/2}\sum_{s=1}^{\infty}s^{-3/2} \qquad (24)$$

Above this temperature, equation (23) is satisfied by a value of λ definitely less than unity, and the first term is negligible. Below this temperature, the solution of (23) is of the form $\lambda=1-\theta/N$, where θ is a fraction, and the first term becomes comparable with the series. The first term really represents the occupation number of the very lowest level ($p=q=r=1$) and λ can never actually attain the value unity, or the occupation number of this very lowest level would be infinite. On the other hand, if T is less than the value T_c given by equation (24), the convergence of the series in (23) (even for $\lambda=1$) implies that no value of λ satisfying (23) could be found without taking the first term into account.

Investigation of the nature of the singularity (F. London (1938)) shows that it leads to a discontinuity in the *third* derivative of f with respect to T at $T=T_c$, that is a discontinuity in $(\partial C_v/\partial T)$ where C_v is the specific heat. Inserting in (24) the mass of an He atom for m, and for N/V a value corresponding to the observed density of liquid helium, we find for the transition temperature the value 3·1°K, compared with 2·2°K for the actual liquid He. The calculated and

observed specific heat anomalies are shown roughly in fig. 69 and it will be seen that the agreement is extremely encouraging considering how crude our model (complete neglect of the actual interactions) really is. If we suppose that the actual distribution of energy-levels differs somewhat from that for a perfect gas, there is no difficulty in obtaining complete agreement with the observed specific heat, F. London (1939). For an account of such improved models, which attempt to take some account of the interactions but retain the assumption that the assembly can be described sufficiently accurately by "one-atom" wave functions, the reader is referred to the original papers. Fraser (1951 a, b), Prigogine and Philipott (1952; 1953 a, b), Zilsel (1953). It should also be mentioned that, strictly speaking, the ordinary methods of statistical mechanics fail when applied to these models, as was pointed out by Schubert (1946), but the truth of

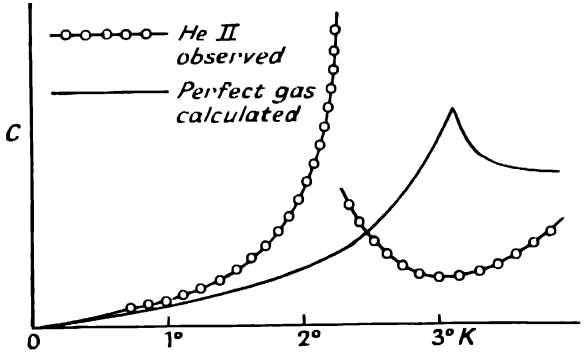

Fig. 69. Relationship between specific heat of He II and calculated anomaly for perfect gas of same density.

equations like (22)–(24) can be established, for certain classes of model, by more elaborate methods. Fraser (1951 a, b), Temperley (1949), Landsberg (1953), Haselgrove and Temperley (1954). It turns out that the accepted results are correct for most cases likely to occur in practice.

It is extremely tempting to identify the situation described by equation (23) with the two-fluid model of liquid IIe, the atoms "condensed" into the lowest level being identified with the superfluid. In fact Zilsel (1953) has shown that a slight generalisation of the perfect gas model *is* capable of accounting for some of the remarkable properties of the superfluid, the atoms in the very lowest level being "left behind" even though the atoms in all the other levels are given a drift velocity less than a certain value. In other words, certain assemblies can be in metastable equilibrium even if there is this relative motion. The atoms in the lowest level must certainly have entropy zero, and it can be shown

that their wave-functions may also be extremely sensitive to applied external fields such as gravity, Lamb and Nordsieck (1941), Halpern (1951). Very strong evidence for the theory that the transition of liquid He is in some way related to this condensation phenomenon is provided by the fact that no such transition occurs in the light isotope He_3, at all events down to 0·25°K. (See p. 316.) This strongly suggests that the transition is connected with the fact that He_4 atoms are described by symmetrical wave functions, in contrast with the antisymmetrical wave functions for He_3.

For a more detailed survey of theories of this type, see the review article by Dingle (1952).

10.6.3. The Debye-like Model at very low Temperatures

An entirely different method of arriving at a model of two-fluid type has been developed by Landau (1941; 1947). We consider an assembly consisting of quantised sound-waves enclosed in a vessel, and enquire what might be expected to happen if one side of the vessel were moved in its own plane, or if a solid were moved through the assembly in such a way that the liquid in the neighbourhood is in statistical equilibrium with the moving solid. This provides a reasonable idealisation of an "oscillating-disc" type of experiment, or of a "capillary-flow" experiment, if we consider the latter type of experiment from the point of view of an observer moving with the liquid. The results that we shall now derive can be obtained in a number of different ways. All of them seem to be based on the assumption that sound-waves carry *momentum* as well as energy, and, indeed some such assumption is already required in order to account for the fact that a sound-wave exerts pressure when reflected at a boundary. The conception of a quantised sound-wave, or "phonon", has no definite meaning except as a property of quite a large number of atoms (for example, the "small volume" of liquid that one customarily considers in hydrodynamics, which nevertheless contains a large number of atoms). In addition to the phonons, which describe both the interactions between atoms and their *relative* motions, it is also necessary to introduce some variable describing bulk motion of the liquid. Thus, local compressions and expansions are described by means of phonons, while, we must associate with each small volume a velocity, describing the motion of its centre of gravity. This fact has been pointed out explicitly by a number of workers, but it is not actually mentioned in Landau's own treatment (1941), though it seems to be implicit in it. The statement that phonons "carry" momentum has to be interpreted carefully. If we have any assembly of interacting atoms, we *can* split it up into normal modes, but all the momentum resides in the one mode associated with the motion of the centre of gravity of all the atoms. However, the creation or destruction of phonons

by collision in general results in a change in the total momentum of the associated atoms (see Penrose (1954)), so it is, in practice, sufficiently accurate to think of the momentum as "carried" by the phonons. See Kronig and Thellung (1950), Temperley (1952 a, b) (1953), Dingle (1952).

If we consider an assembly of atoms and phonons from the standpoint of an observer moving relatively to it, the energies of the phonons that are moving in his direction seem to him to be lower than they would to an observer at rest relative to the assembly, while the energies of similar phonons moving in the direction opposite to his direction of motion will seem higher to him than to a stationary observer. If the relative velocity is $\mathbf{v}$, the corresponding change in the energy of a phonon of frequency ν will be, as a consequence of the Doppler effect,

$$\Delta E = v h\nu \cos\theta/c_1 = \mathbf{p}.\mathbf{v} \tag{25}$$

where θ is the angle between the velocity $\mathbf{v}$ and the direction in which the phonon is travelling, and $\mathbf{p}$ represents the momentum "carried" by the phonon. The magnitude of this vector has to be taken equal to E/c_1, in order to obtain a consistent picture of an assembly of phonons, for example, in order to get the correct acoustic pressure on a boundary. Equation (25) can also be derived, for example, from Hamilton's equation $\mathbf{v} = \partial H/\partial \mathbf{p}$ leading to $H = H_0 + \mathbf{p}.\mathbf{v}$.

We consider the consequences of equation (25) and suppose that the liquid in the neighbourhood of a solid body moving through it with a velocity v is in thermodynamic equilibrium with that body. In particular, we can compute the mean momentum "carried" by unit volume of this liquid, as a consequence of equation (25) which makes phonons moving *with* the solid body somewhat more frequent than phonons moving in the opposite direction. Because of the relation between carried momentum and frequency, the customary enumeration of phonons by wave vector is equivalent to their enumeration by momentum vector. The number of normal modes of sound per unit volume, having a wave vector whose magnitude lies between k and $k+\mathrm{d}k$ is

$$\frac{1}{8\pi^3}\int_0^{\pi}\int_0^{2\pi} k^2 \mathrm{d}k \sin\theta \mathrm{d}\theta \mathrm{d}\phi \quad \text{or} \quad \frac{1}{h^3}\int_0^{\pi}\int_0^{2\pi} p^2 \mathrm{d}p \sin\theta \mathrm{d}\theta \mathrm{d}\phi$$

We may take the axis of θ in the direction of the velocity $\mathbf{v}$. The number of quanta per unit volume, specified by a momentum vector whose magnitude lies between p and $p+\mathrm{d}p$ is, using Planck's expression and taking account of (25),

$$\frac{2\pi}{h^3}\int_0^{\pi} p^2 \mathrm{d}p \sin\theta \mathrm{d}\theta \frac{1}{\exp\{(pc - pv\cos\theta)/kT\} - 1} \tag{26}$$

The total momentum "carried" by these quanta along the direction of **v** is, per unit volume,

$$\frac{2\pi}{h^3}\int_0^{\pi}\int_0^{\infty}\frac{p^2\mathrm{d}p\,\sin\theta\mathrm{d}\theta\,.pv\cos\theta}{\exp\{(pc-pv\cos\theta)/kT\}+1} \tag{27}$$

the momentum in other directions vanishing by symmetry. This expression is readily shown to be equal to

$$\frac{16\pi^5k^4T^4}{45h^3c^3}v+\mathrm{O}(v^3) \tag{28}$$

Thus, the solid moving through the liquid has apparent extra momentum as a result of its encounters with the phonons in the liquid, and it will, for example, need a correspondingly larger force to change the velocity **v** than it would in the absence of the liquid.

Now, this may be interpreted as meaning that the motion of a solid body through the liquid is associated with an "effective density" of the liquid, arrived at by dividing expression (28) by v. It is Landau's proposal (1941) to identify this "effective density" with the "density of normal fluid" ρ_n used in the two-fluid picture, at temperatures such that this effective density is less than the actual density of liquid. For a solid moving through an *ordinary* liquid, the layer of liquid in immediate contact with the solid is carried along entirely, and the effective density is equal to the actual density. (As we recede from the solid, the fact that the viscosity of the liquid is finite of course results in the successive layers of liquid slipping past one another. In a "phonon" or similar type of picture, such a situation is described by saying that the phonons have a finite mean free path.)

It is possible to perform calculations on the same lines as these summarised by equations (26)–(28) for the transport of energy and entropy (Dingle (1952)). As we might expect, the assumption that the solid is in statistical equilibrium with the neighbouring layers of liquid is found to imply that their entire energy and entropy is transported with the velocity v, even though the effective density deduced from equation (28) may be less than the actual density of the liquid, in other words, not all of the *mass* of the liquid is transported with this velocity. Thus we are led, by another path, to a model on which a "two-fluid" picture can be based.

A similar set of results can be deduced from the same model by a different approach, due originally to Ward and Wilks (1951; 1952). According to this picture the phonons are treated as particles that are capable of colliding with and scattering one another. This involves introducing a mean free path, a relaxation time, or some equivalent concept, but something of this kind is already needed to describe the ordinary phenomena of viscosity in a liquid and thermal conductivity

in a liquid or solid. Each element of the liquid then contains, in equilibrium, a number of phonons (of any given frequency) per unit volume that depends on the temperature only. The finite mean free path of the phonons then results in a transport of heat from regions of high to low temperatures, the ordinary mechanism of heat conduction in a solid, Peierls (1929). If however, fluctuations of temperature occur with a wavelength long compared with this mean free path, or, put in another way, with a frequency low compared with the inverse relaxation time associated with the restoration of equilibrium, the process of restoration of temperature equilibrium will take place reversibly. By applying the principles of conservation of energy and conservation of momentum to the phonon gas, Ward and Wilks (1951; 1952) succeed in deducing both the result $c_2 \approx c_1/\sqrt{3}$, Landau (1941), and the accepted expression (2) for thermomechanical effect without explicit reference to a two-fluid picture. These results are only expected to be valid in a certain temperature region for which:

(a) The mean free path of the phonons is not too long (i.e. the "phonon gas" is not in the "Knudsen" region, so that it is sensible to speak about the temperature of the phonons in a small volume of liquid).

(b) The number of "umklapp" processes (Peierls (1929)) is small. (This proviso is necessary because "umklapp" processes result in the conservation of momentum becoming inapplicable to an assembly of sound quanta.)

Indeed, we find experimentally that Landau's limiting result is only valid over a small range of temperature. This discussion is of interest in that it shows that the two-fluid conception may eventually be replaced, but no one has so far suggested a workable means of avoiding it in discussing the variation of c_2 between 1 °K and the λ-point. The Ward and Wilks treatment can be extended to other assumed energy-spectra besides the pure phonon one, Dingle (1952). It should be mentioned that assumption (a) about the mean free path of phonons is not in conflict with observed results on the easy transmission of ordinary sound in liquid helium, Chase (1953), because the frequency of sound accessible experimentally at present, up to about 10^8 c/sec, is still small compared with that of the sound quanta in which most of the thermal energy resides even at temperatures as low as 0·5 °K. This frequency is $kT/h \approx 10^{10}$ c/sec. Chase's work (1953) gives evidence about the possible dependence of mean free path and relaxation time on frequency.

As we have seen above (p. 289), there is a definite tendency for the observed velocities of propagation of pulses of second sound to approach c_1 rather than $c_1/\sqrt{3}$ as $T \to 0$. Such an occurrence would be expected if, for example, the *true* heat conductivity or the viscosity of the normal

fluid were becoming *large* as $T \to 0$, for this would lead to the modes corresponding to first and second sound becoming coupled (p. 294). However, the statement that either, or both, of these quantities is approaching large values is equivalent to the statement that the mean free path of the phonons is also approaching large values. In this case we have to consider the alternative possibility that, as in the Knudsen gas, the concepts of heat conductivity and viscosity may become *inapplicable*, collisions of phonons with the walls becoming the dominant mechanism. Finally, in the limiting case of a tube of very large radius, phonons would travel directly from heat source to thermometer without any collisions at all, and the observed velocity of propagation of second sound would then approach c_1.

Up to the present, it has not been possible to decide between these two possibilities, although they are in reality quite distinct. The appearance of coupling terms in the two-fluid hydrodynamics should lead to observed pulse-distortion and propagation velocities that are independent of the geometry. It is, for example, easily shown that the introduction of a dissipative term into the equation of propagation of second sound can account for received pulses of the type observed by Atkins and Osborne (1951), and such terms also give rise to a coupling between first and second sound. On the other hand Ziman (1954) has shown that pulses of this type can also be accounted for if the mean free path is becoming long though, in this case, the effect should vary strongly with the geometry. Various workers, e.g. Atkins (1953 a), Mayper and Herlin (1953), have suggested that mean free path effects are involved, and the calculations of Khalatnikov (1952) give some support to this idea. (For an "ideal" phonon gas the mean free path would, of course, be infinitely great because the sound-waves are then the correct normal modes of the assembly.)

It seems to the author entirely possible that, at temperatures of the order of 0·2°K, the rapid increase of mean free path with falling temperature that is to be expected on almost any theory based on a "solid-like" model may, in this instance, lead to the situation that the "volume" dissipative terms become important and "Knudsen" effects become important in *almost the same temperature range*. Such an assumption is very plausible numerically, but it would make exact analysis of pulse-type measurements extremely difficult. We have already mentioned above (p. 287) the possible intervention of mean free path effects in very narrow channels ($\sim 10^{-4}$ cm) which is suggested by analysis of pseudo-heat conduction experiments at "high" temperatures, where the mean free path would be correspondingly shorter.

The phonon model has been developed considerably further. In the first place, longitudinal sound-waves are not a complete description of the interactions and relative motions of the atoms. In a solid, the missing

normal modes are represented by transverse or shear waves, but the corresponding degrees of freedom for a liquid are not known. Landau (1941) began by assuming that they could be represented by quantised vortex motions, "rotons", which were supposed to be endowed with a definite effective mass and momentum. A somewhat similar idea was proposed by Onsager (1949). Later (1947) Landau assumed a definite energy-momentum spectrum, similar to that of a solid, made up of two portions (fig. 70),

$$E=c_1 p, \qquad E=\Delta+\{(p-p_0)^2/2\mu\} \tag{29}$$

and carried through further calculations on the lines already described for the phonon model with adjustable constants Δ, μ and p_0. The second branch of the spectrum only becomes appreciably excited at temperatures above about 0·6°K, but the precise physical meaning of the parameters is largely left unspecified. Landau and Khalatnikov

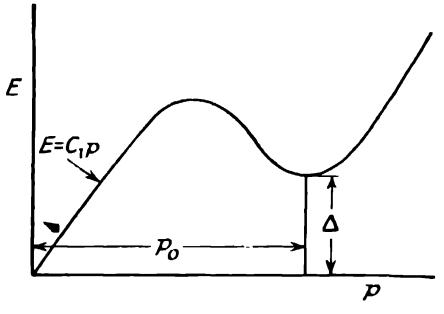

Fig. 70. Relation assumed by Landau between energy and momentum of elementary excitations.

(1949 a, b), Khalatnikov (1950; 1952), have attempted to calculate the mean free paths associated with various types of scattering process, and succeed in getting reasonable agreement with much of the experimental data, but it is by no means certain that some of the possible scattering processes *not* considered by them are not also of importance. See, for example, Kramers (1952). At temperatures in the He II region, the precise way in which the two branches of the spectrum (29) are "joined up" is immaterial. We could assume a cusp, or even a forbidden range of values of p, without altering the thermodynamic consequences of the model, which depend mainly on c_1 and on the shape of the spectrum near the minimum.

For a comparison of the successes and failures of the "solid-like" and "gas-like" models, the reader is referred to papers by Temperley (1952 a) and Dingle (1952). Very briefly, it seems clear that neither picture is completely satisfactory, but that the "solid-like" picture is better near absolute zero, and the "gas-like" picture is better near the

transition temperature. In its present form, the "solid-like" model fails altogether to predict a transition. Since the energy-spectrum (29) is not unlike that for an ordinary solid or liquid, we are left in doubt as to how the liquids He I and He II are supposed to differ, or why a spectrum such as (29) suddenly ceases to be valid at a transition temperature, as Landau (1941) suggests, and why the transition occurs just when $\rho_n/\rho=1$.

10.6.4. Approaches based on the Two-atom Distribution Function

This approach was first tried by Born and Green (1947; 1948). In view of its undoubted successes with the classical liquid, this approach might be expected to be very fruitful, particularly for this case, which seems to fall in the awkward intermediate range for which neither "gas-

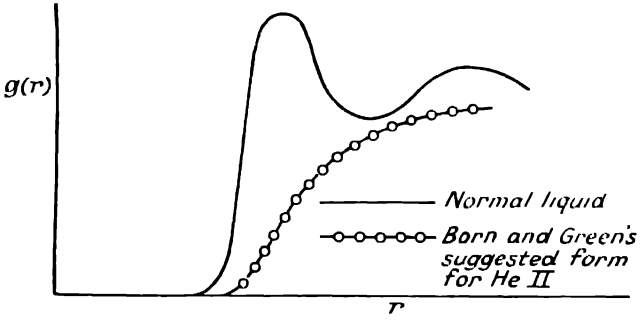

Fig. 71. Born and Green's suggested form of distribution function for liquid He II.

like" nor "solid-like" models are particularly good first approximations. Considering two atoms explicitly would be expected to be decidedly better than considering a single atom moving in some "effective field" representing the effect of the remaining atoms. Born and Green (1947; 1948) based their theory of liquid helium on two main premises:

(a) A solution of the problem of the interaction of two helium atoms led to the conclusion that, at very low temperatures, the two-atom distribution function should differ considerably from that characteristic of a classical liquid. See fig. 71. They argued that the existence of superfluid properties was in some way connected with this fact. However, no very noticeable change occurs in the observed X-ray scattering as we pass through the transition temperature, so that superfluid properties are already in evidence when the distribution function still resembles that of a classical liquid, Reekie and Hutchison (1953).

(b) That there are two possible definitions of pressure in a liquid the "thermodynamic" ($P=-(\partial E/\partial V)_s$), and the "hydrodynamic"

(based on the equation $\rho \mathrm{d}v/\mathrm{d}t = -\mathrm{grad}\, P$) and that these are not equivalent in a quantum assembly. The difference between these two pressures acts as an additional parameter in the hydro-thermodynamic equations and enables one to deduce results very like those given by the "two-fluid" picture. This suggestion led to a controversy, see Price (1950) for a survey and discussion.

Unfortunately, this controversy seems to have obscured the potential value of the approach based on the distribution function. For example, Penrose (1951) pointed out that the following assumption about the density matrix $\rho(x_1, x_1')$, which is closely related quantum-mechanically to the distribution function for two or more atoms, would lead to the two-fluid model as a natural consequence:

$$\rho(x_1, x_1') \nrightarrow 0 \quad \text{as} \quad |x_1 - x_1'| \to \infty \tag{30}$$

the result actually assumed being a finite oscillation as $|x_1 - x_1'|$ becomes large. This assumption may be regarded as a statement of the existence of long-distance correlation between the positions of any two atoms in the enclosure. This is an extremely plausible consequence of an interaction near the critical value necessary to give a bound level. If, for example, we had just two atoms in an enclosure, and they had an interaction of just the critical value, their combined wave function in a one-dimensional enclosure would only vary very slowly with their distance apart, and, in a three-dimensional enclosure, would only vary like $A(r_{1,2})/r_{1,2}$ where $A(r_{1,2})$ is a slowly varying function. See fig. 67. Very recently Feynman (1953 a, b, c) has also pointed out that a condensation resembling that of a perfect gas will occur if the Fourier transform of the distribution function has a singularity at the origin of a certain type, which is practically equivalent to assumption (30), and is also closely related to the assumption finally made by Temperley (1953) in an attempt to compromise between the "gas-like" and "solid-like" models, the mechanism assumed being the formation of "small clusters", that is to say long range correlation between the motion of comparatively small numbers of atoms. We have already noted above the close relationships between the concepts of "cluster" and "distribution function" (pp. 88–89).

Another fruitful application of the "distribution function" technique has been tried by A. Bijl (1940), Onsager (unpublished), Price (unpublished) and Feynman (1954). The technique is to attempt to construct wave functions of the type

$$\Psi = \phi \sum_n \exp\,(i\mathbf{K}.\mathbf{r}_n) \tag{31}$$

where $\mathbf{r}_n$ is the position vector for the nth atom and ϕ is the wave function representing the ground level, which is left unspecified. If we substitute such a wave function into the many-body wave equation,

the interaction energies disappear, because ϕ itself satisfies the wave equation, and, after substituting Ψ into the wave equation and carrying out the steps indicated by Feynman (1954), we reach the conclusion that if excited levels can be represented by a wave function such as (31) their energies must be given by an expression of the form

$$E(K)=E_0+\frac{h^2\mathbf{K}^2}{8\pi^2 mS(K)} \tag{32}$$

where E_0 is the energy of the ground level and $S(K)$ is simply the Fourier transform of the distribution-function, since $\Psi\Psi^*$ when integrated over the co-ordinates of all but two of the atoms represents, by definition, the probability of finding two atoms in specified positions. Now this quantity $S(K)$, the transform of the distribution function, is also what is measured by an observation of X-ray or neutron scattering; see, for example, Frenkel, *Kinetic Theory of Liquids* (1946). This means that, until better methods of handling the quantum-mechanical many-body problem become available, we can abandon the attempt to calculate the distribution function from the interaction energy or vice versa, and regard the information obtained from X-ray or neutron scattering as the fundamental data to be used in computing an approximate set of energy-levels (33) and we can then use these to set up a partition function.

The behaviour of the function $S(K)$ is of course not completely known, but, if it may be supposed that it is linear at the origin, expression (33) will lead to a set of energy levels qualitatively the same as those assumed empirically by Landau (1947) (fig. 70), the assumed minimum in the function $E(K)$ being caused by the maximum in the function $S(K)$ associated with the first liquid ring in the observed diffraction pattern. The range of validity of this process for computing the lower part of the energy spectrum is not known, and rests on that of approximate wave functions of the type (31). Feynman (1954) has shown by a variational method that the imaginary exponential is the "best possible" function that can be used in this way, in the sense that it is the type of function that gives the lowest value for a given excited level, and therefore is the nearest approach that one can make to an exact wave function within the framework of assumptions of the type (31) (arrived at by multiplying the (unknown) ground-level wave function ϕ by a reasonably simple "trial function").

Only preliminary calculations have so far been carried out, but this approach appears to be extremely promising. By adding to it the further assumption that $S(K)$ has a singularity of suitable type at the origin, which, as we have seen, is a reasonable consequence of the interaction being near the critical strength, we can arrive at both a physical basis for the two-fluid picture (p. 313) and an explanation of the transition

which is a generalisation of the transition that occurs in the perfect gas. This supposed behaviour of the function $S(K)$ would not be directly observable in a scattering experiment, in line with the observed fact that no big jump occurs in the scattering as we pass through the transition temperature. The fundamental mistake that seems to have been made by Landau and Khalatnikov (1947; 1949 a, b; 1952) is that they chose their parameters in such a way as to account for the *whole* specific heat of He II. Now the whole specific-heat curve of liquid helium strongly resembles a Debye curve, with a typical λ-type anomaly *superposed on it* (fig. 72), and it is significant that the Debye Θ that one calculates on the basis of the specific heat of He I is practically identical with that which is required to interpret the specific heat of He II at "low" temperatures (below about 0·6° K) and with the Debye Θ that follows from the observed "low" temperature value of the velocity of sound c_1.

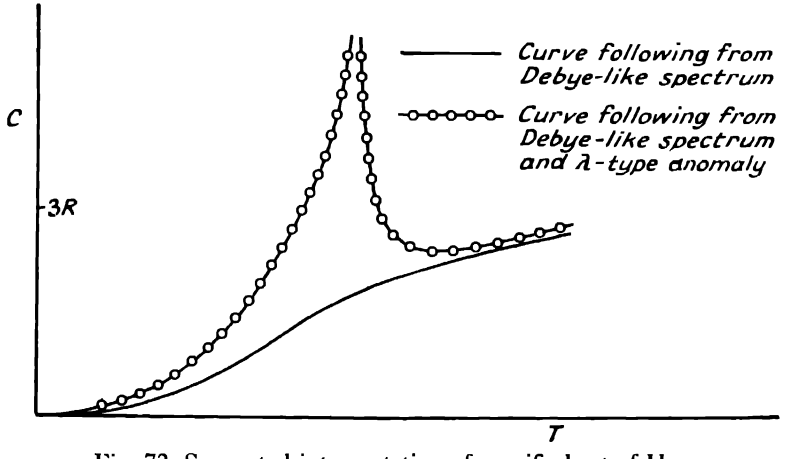

Fig. 72. Suggested interpretation of specific heat of He_4.

One is thus led to the idea that the actual excitation spectrum of the liquid does depart from the simple Debye model (as indeed occurs even for an "ideal" solid) but that the departure is not as great as that assumed by Landau and Khalatnikov, and thus "room" can be left on the calculated specific-heat curve to accommodate the specific-heat anomaly associated with the transition. As data on X-ray and neutron scattering become available calculations of the expected spectrum on the lines indicated by equations (31)–(32) will clearly be of very great interest. Should this expectation about the excitation spectrum be verified it will then be possible to say that almost all the approaches to a theory of liquid helium have been successfully synthesised, and that we now know the physical basis of the "two-fluid" model. (This would still leave outstanding the difficult problem of accounting for the various "critical velocities" at which superfluid effects are modified or cease.)

10.7. The Properties of He_3

The He_3 isotope is still only available in small quantities, and many of its properties are not yet known. It has been established that it has a melting-curve similar to that of He_4 and that the liquid phase almost certainly persists down to absolute zero, Abraham, Osborne and Weinstock (1952), though the behaviour of the melting curve below about 0·5°K is unknown (the melting pressure may even pass through a minimum). The vapour-pressure curve has been measured by Sydoriak, Grilly and Hammel (1949) and also by Abraham, Osborne and Weinstock (1953 a) and seems to resemble that of a normal liquid. Recently, measurements of the specific heat have also been made, Sydoriak and Roberts (1953), Abraham, Osborne and Weinstock (1953 b), Daunt and de Vries (1953; 1954). Naturally, a search has been made for evidence of superfluidity or of some transition resembling that in He_4 occurring in the liquid, but the evidence at present available appears to be against such happenings. For a review of the earlier work see Daunt (1952). A transition to some *antiferromagnetic* configuration as a result of exchange effects remains possible, but there seems no particular reason for expecting *superfluidity* in the low-temperature modification. It is known that no transition occurs above 0·25°K. Analysis of the specific heat data, and of the magnetic resonance measurements of W. M. Fairbank *et al.* (1953), shows that, at 0·5°K, nearly all the entropy of the liquid is associated with "spin-disorder", and that, at 0·4°K, the formation of some ordered configuration of the spins has definitely begun.

The general picture is consistent with what might be expected of an assembly of atoms obeying Fermi statistics, the density of the liquid presumably being fixed, as in He_4 by a balance between attractive forces and zero-point energy. It is not surprising that the zero-point energy is even more important than in He_4, so that the equilibrium density of liquid He_3 is only about 0·08 gm/cm^3, only just over half that of He_4. Very recently Temperley (1955) has shown that the simple cell model of a liquid can be developed in a natural way to describe the observed properties of liquid He_3 with surprising quantitative accuracy. It is natural to ask whether the properties of the actual liquid at all resemble those of the hypothetical Fermi gas. Unlike the Bose gas, such an assembly would have a finite zero-point energy and compressibility even in the absence of any interaction at all between the molecules. Inserting the observed density of the liquid into the standard formulae, one arrives at a Fermi temperature of 4·85°K, but a specific heat and entropy that agree only qualitatively with observation. One can try to take rough account of the distortion due to the interatomic interaction by introducing corrections of van der Waals type, Temperley (1954),

and this leads to a rough model which describes *both* changes of state in the semi-quantitative manner typical of theories of van der Waals type. Since the effect of Fermi statistics makes the atoms avoid one another in any case, it seems that extremely crude treatments, which would fail completely for He_4, can give worth-while results. Similar very crude models have had important successes in describing the properties of metals, and of atomic nuclei, perhaps for the same sort of reason. For a review of the properties of He_3 that seem to be consistent with this conception of a "distorted" Fermi gas the reader is referred to Temperley's (1954) and Daunt's papers (1952).

The behaviour of He_3/He_4 mixtures has also been the subject of considerable study (see Daunt's paper for a review (1952)). Some of the earlier experiments are difficult to interpret because film phenomena made satisfactory vapour-pressure measurements difficult, and also because of a strange new phenomenon usually referred to as the "heat-flush" effect, namely that a flow of heat through a mixture leads to "pseudo-heat conduction" as usual, but also results in the *transfer* of the He_3 atoms *in the same direction as the heat flow*. (This effect can, in fact, be made the basis of workable methods of enriching an He_3/He_4 mixture.) It was predicted by Pomeranchuk (1949) that "foreign" atoms in He_4 would travel with the normal fluid and not participate in the motion of the superfluid. On this basis, the two-fluid hydrodynamics can be generalised simply by supposing that the mass of He_3 per unit volume has simply to be added to the density of normal fluid ρ_n.

That "foreign" atoms should be transported by the "normal fluid" as a consequence of the identity principle is plausible enough. The wave function describing the motion of x He_4 atoms and one foreign atom would be quite different from that describing $(x+1)$ He_4 atoms, even if the interaction energy were the same, but no one has yet shown unambiguously that the symmetry properties of the wave functions *must* lead to such a result. It would, for example, be equally consistent with anything that is known theoretically or experimentally if the He_3 atoms moved with a velocity that is some fraction of v_n. (The assumption that the He_3 atoms move with the *centre of gravity* of each small volume of He_4 seems incompatible with the "heat-flush" effect.) A very recent experiment, Guttman and Arnold (1953), seems to indicate that He_6 atoms also do not participate in superfluid motion in He_4. These atoms should obey Bose statistics but, in small concentration in He_4, should equally behave as "foreign" atoms.

10.8. The Entropy of Mixing

One further piece of information is needed before the two-fluid "hydro-thermodynamics" can be set up for the general case of He_3/He_4

solutions, namely some means of estimating the entropy of the solutions. One assumption that might be made, usually known as Taconis' hypothesis, is that we are to compute the entropy of mixing as if the He_3 mixed only with the normal fluid, i.e. just as if the superfluid were not present at all. de Boer and Gorter (1950) have based their extended form of the two-fluid model on this idea. A somewhat simpler idea is due to Heer and Daunt (1951), who use the simple "smoothed-potenial" model for both liquids (see p. 72), the interactions between atoms being represented simply by supposing all the He_4 atoms to be moving in a potential "well", making a similar assumption for the He_3 atoms, and then computing the expected behaviour of a perfect mixture of two such gases.

These theories can, apparently, be subjected to fairly extensive tests, because data is becoming available in at least three independent ways:

(a) On the variation of the position of the λ-point with composition.

(b) On the variation of the partial vapour-pressures of the solutions with temperature and composition.

(c) On the variation in the velocity of second sound in the mixtures with temperature and composition.

The predictions of the various theories that have been proposed do not differ very greatly, and it seems that fairly extensive experimental data on these lines will be needed. Nanda (1954) has suggested that measurements of heats of solution might give a more sensitive check between the different assumptions.

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